CONTRIBUTIONS TO ALUMINUM CHLORIDE IN ORGANIC CHEMISTRY

Part I. CONDENSATIONS OF ALIPHATIC ALCOHOLS WITH PHENOL AND WITH BENZENE OR ITS HOMOLOGS.

Part II. REARRANGEMENT OF BENZYL PHENYL ETHERS.

A DISSERTATION

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for the Degree of Doctor of Philosophy

by
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FOREWORD

Kranzlein's "Aluminiumchlorid in der organischen Chemie" has been revised in 1932. This dissertation may be considered to be two contributions to that monograph. Parts of both Part I and Part II have been presented at the Cleveland and Indianapolis meetings of the American Chemical Society in 1934 and in 1931, respectively.

To Dr. R. C. Huston, Dean of Applied Science and Professor of Organic Chemistry of Michigan State College, the writer is indebted for suggestions and encouragement in carrying out this work. The writer also wishes to express his gratitude to Dr. Huston for the personal help given him during the more than two years he has attended Michigan State College.

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Part I.

CONDENSATIONS OF ALIPHATIC ALCOHOLS WITH PHENOLS AND WITH BENZENE OR ITS HOMOLOGS IN THE PRESENCE OF ALUMINUM CHLORIDE.

INTRODUCTION.

In the course of studying the isopropyl phenyl ether rearrangement by means of aluminum chloride in 1933, a condensation of isopropyl alcohol with phenol was carried out in the presence of aluminum chloride with the object of getting the p-isopropyl phenol for seeding purposes which, as recorded in the literature (1), is a solid substance, m.p. 59-60°, b.p. 229-230°. After the usual work-up, a solid substance, m.p. 92-93°, b.p. 234-235°, resulted. A subsequent run was tried by adding isopropyl alcohol to a stirred mixture of aluminum chloride in benzene and it gave a fair yield of cumene. Thus these condensation reactions of aliphatic alcohols with phenol and with benzene in the presence of aluminum chloride were discovered.

REVIEW OF LITERATURE.

In 1926 Huston and Sager (2) reported the condensation of allyl alcohol with benzene in the presence of aluminum chloride to give a 16% yield of allylbenzene. They concluded that under the reported experimental conditions saturated aliphatic alcohols such as methyl, ethyl, n-propyl, etc., do not condense with benzene in the presence of aluminum chloride. Neumann (3) reported the condensation of allyl alcohol with phenol by means of aluminum chloride in his M.S. thesis, 1933.

In 1920 Huston (4) discovered that aromatic alcohols such as benzyl alcohol reacted with phenol in the presence of aluminum chloride to give a good yield of p-benzyl phenol. Later Huston co-workers (5) showed that aromatic secondary alcohols such as benzhydrol, phenyl methyl, phenyl ethyl, and phenyl n-propyl carbinols also reacted with phenol in the presence of aluminum chloride to give the corresponding para substituted phenols. The condensation of an aromatic tertiary alcohol like triphenyl carbinol and phenol in the presence of aluminum chloride has not yet been reported.

This Huston method of using aluminum chloride to condense benzyl or halogenated benzyl alcohols with phenol or halogenated phenols, cresols or halogenated cresols constitutes many publications by Huston and co-workers (6).

In 1897 Nef (7) mentioned the formation of diphenylmethane from benzyl alcohol and benzene in the presence of aluminum chloride. In 1916 Huston and Friedmann (8) reported a 30% yield of diphenylmethane among other products from the reaction of benzyl alcohol and benzene in the presence of aluminum chloride. They further reported that aromatic secondary alcohols such as benzhydrol, phenyl methyl and phenyl ethyl carbinols also reacted with benzene in the presence of aluminum chloride to give the corresponding hydrocarbons with good yields. Aromatic tertiary alcohol like triphenylcarbinol reacts with benzene in the presence of aluminum chloride to give triphenylmethane and not tetraphenylmethane (9).

Again, Huston (4) showed that anisole and phenetole acted like benzene in that they condense with benzyl alcohol to give the para substituted benzyl anisole and phenetole.

All these condensations of aromatic and unsaturated aliphatic alcohols with aromatic hydrocarbons and phenols by means of aluminum chloride indicated that unsaturation of the alpha carbon atom, whether it be double bonded or a member of the benzene ring favors condensation.

Very recently Huston and Coodemoot (10) reported the condensations of a few cycloalkyl carbinols with benzene in the presence of aluminum chloride.

METHODS OF PREPARING ALKYL PHENOLS.

One method of preparing alkyl phenols was discovered in 1867 by Kekule and Wurtz, independently. It consists of the first step of sulfonating the alkylbenzene and then fusion with KOH (11). Another method involves the nitration of the alkyl benzene, reduction of the nitro into the amino compound, the diazotization of the amino compound and hydrolysis to the phenol (11) (12). This method was used in this paper to synthesize the three tertiary hexyl phenols from the three tertiary hexyl benzenes (see Experimental).

Phenols, under the influence of concentrated sulfuric acid, take up unsaturated hydrocarbons to form alkyl phenols. Thus in 1933 a patent (13) described the formation of secondary hexyl resorcinol from 2-hexene and resorcinol under the influence of 90% sulfuric acid.

Phenols and alcohols condense to form alkyl phenols under the influence of 70-80% sulfuric acid (14).

In 1934 Chichibabin (15) used phosphoric acid as a condensing agent for the preparation of alkyl phenols from phenols and alcohols.

Concentrated perchloric acid has been used to condense aliphatic alcohols with phenols to form alkyl phenols (16).

The use of zinc chloride to condense phenols and alcohols is well known (17). Magnesium chloride and alkali bisulfates act similarly (18).

The Friedel and Crafts reaction is also used to prepare alkyl phenols. Instead of aluminum chloride ferric chloride can be used as a condensing agent (19).

Pyman and co-workers (20) in 1930 reported the preparation of a series of alkyl phenols. They first prepared the phenyl esters and then through the Fries rearrangement the acyl phenols were made. Finally the phenols were obtained from the reduction of the acyl phenols by the Clemmensen method.

Johnson and students (21) started the preparation of a series of higher alkyl phenols by using the Nencki condensation and the Clemmensen reduction method. The Nencki condensation involves the use of zinc chloride to condense an aliphatic acid with phenol. The resulting acyl phenol was then reduced to the alkyl phenol by the Clemmensen method. In this way the useful hexylresorcinol was first prepared.

Finally the Claisen reaction (22) is also used to prepare alkyl phenols. The formation of alkyl phenols from the rearrangement of phenol ethers by means of heat (23), sulfuric and glacial acetic acids (24), boron fluoride (25), zinc chloride or HCl (26), and aluminum chloride (27) should be mentioned.

METHODS OF PREPARING ALKYL BENZENES.

For the preparation of alkyl benzenes there should be mentioned the polymerization of alkyl acetylenes (29), the reduction of phenols by means of zinc dust (28). The use of zinc alkyls and benzal or benzyl chlorides was also reported for the preparation of alkyl benzenes (30). Dry distillation of an aromatic acid with lime or soda lime is also used. It was by this method that isopropyl benzene or cumene was first prepared from cumic acid (31).

However the most frequently used methods are the Fittig synthesis discovered in 1864 (32) and the Friedel and Crafts reaction (33) discovered in 1877.

The Grignard reaction is very frequently employed. Thus a very good yield of n-propylbenzene obtained from the reaction of benzylmagnesiumchloride and diethyl sulfate has been described in Organic Syntheses (34). Alkylene benzene derivatives made from the Grignard reaction can be reduced to the alkylbenzenes (35).

Verley (36) used 30% fuming sulfuric acid to condense isobutyl alcohol and benzene to form tertiary butyl benzene. Meyer and Bernhauer (14) reported the use of 70-80% sulfuric acid to condense alcohols and benzene or its derivatives.

DISCUSSION.

Of the aliphatic primary, secondary, and tertiary alcohols it was found that only the tertiary alcohols condense with phenol in the presence of aluminum chloride to give good yields of p-tert.-alkyl phenols. The condensation product of isopropyl alcohol and phenol which initiated this new field has not been identified as yet. The other secondary alcohol tried was sec-butyl alcohol and it did not condense with phenol. Primary alcohols such as n-propyl and n-butyl alcohols also did not condense with phenol.

The condensations were carried out by using a technique Huston used in the condensations of aromatic alcohols with phenols.

Of the five p-tert.-alkyl phenols here prepared only the p-tert-butyl and p-tert-amyl phenols are known. The three p-tert-hexyl phenols were analyzed for carbon and hydrogen by combustion. The para positions of the three tert-hexyl groups were determined through syntheses. First the three tert-hexyl benzenes were prepared and then nitrated according to Malherbe's method (12) to get the p-nitro-tert-hexylbenzenes. The para position of the nitro group was determined by oxidizing the tert-hexyl group with dilute nitric acid (1.20), in a sealed tube heated to 130° for several hours in a Carius combustion furnace, to p-nitrobenzoic acid, m.p. 240°. Next the p-nitro-tert-hexylbenzenes were reduced to the p-amino compounds by means of tin and hydrochloric acid. The amino compounds were diazotized and hydrolyzed to obtain the phenols.

The three p-tert-hexyl phenols thus synthesized were proved to be identical with those prepared from the condensations by mixed melting point determination.

The benzoyl, benzene sulfonyl, and p-toluene sulfonyl esters of the five p-tert-alkyl phenols were prepared by the pyridine method.

All four aliphatic secondary alcohols described here condensed with benzene in the presence of aluminum chloride to give a 25% or better yield of the corresponding alkyl benzenes. Each condensation was carried out by a procedure proposed by the writer. Instead of adding the aluminum chloride to a stirred mixture of alcohol and benzene as is done in the case of aromatic alcohols and benzene or phenol, the alcohol was added slowly to a stirred mixture of aluminum chloride and benzene (see Experimental). In this way the temperature of each condensation can easily be controlled by simply regulating the rate of addition of the alcohol. Furthermore it gives better yields (see Fox's M.S. Thesis) (37). A similar technique has been used by Adams (38) for the preparation of acetophenone.

The four aliphatic secondary alcohols used are dimethyl, methyl ethyl, methyl n-propyl and methyl isopropyl carbinols. The last named alcohol was prepared from a method given in Organic Syntheses (39).

Using the same technique used for the condensations of aliphatic secondary alcohols with benzene in the presence of aluminum chloride, aliphatic tertiary alcohols were found to condense with benzene much more readily and give higher yields than the aliphatic secondary alcohols.

Fox (37), with the knowledge of the writer and using the technique mentioned above, reported the condensations of tert-butyl, tert-amyl alcohols as well as the dimethyl n-propyl and dimethyl isopropyl carbinols with benzene and determined some of the physical constants such as density, indices of refraction, surface tension, molecular volume and parachor of the four tertiary alkyl benzenes thus prepared. Diethyl methyl carbinol condensed with benzene to give a good yield of diethyl methyl phenyl methane.
Tertiary butyl alcohol was found also to condense with toluene, m-xylene, and methyl m-cresyl ether to give the corresponding tertiary butyl derivatives. These tertiary butyl compounds when nitrated gave nitro compounds generally known as artificial musks (40).

Tertiary butyl, amyl, hexyl alcohols like benzyl alcohol were found also to condense with anisole to a very high yield of the corresponding tert-alkyl anisoles. When tert-butyl anisole was nitrated it gave a nitro derivative melting at 100°, indicating that the tert-butyl group entered the para position. The dinitro derivative of p-tert-butyl anisole melts at 100° as recorded in the literature. When dimethyl isopropyl anisole was similarly nitrated it gave a nitro compound melting at 62° and possessing some odor. No further work was done besides these with the tert-alkyl anisoles which were prepared for the purpose of proving the structures of the tert-alkyl phenols.

However it should be mentioned here that they can not be oxidized to anisic acid by means of cromic acid, potassium permanganate, etc. This agrees with the observation of Malherbe (12) using p-nitro-tert-butyl benzene which can not be oxidized to p-nitrobenzoic acid by cromic acid, potassium permanganate, etc.

Aliphatic primary alcohols such as n-propyl and n-butyl alcohols do not condense with benzene in the presence of aluminum chloride.

EXPERIMENTAL.

(I) CONDENSATIONS OF TERTIARY ALCOHOLS WITH PHENOL:

Tertiary butyl and tertiary amyl alcohols were obtained from the Eastman Kodak Co., and the three tertiary hexyl alcohols were prepared by the Grignard reaction. Inasmuch as all condensations were carried out in a similar manner only a typical run is described here.

Twenty-two grams (.25 mole) of tert-amyl alcohol and 23.5 g. (.25 mole) of phenol were treated with 80 cc. of petroleum ether in a 500 cc. three-neck flask fitted with a mercury-sealed stirrer and a reflux condenser which carried both a thermometer reaching to the alcohol phenol mixture and a bent tube for the outlet of the HCl gas evolved. This set-up was placed in the hood. Then 17 g. (.125 mole) of $AlCl_3$ was added to the mixture at such a rate so that the temperature was kept at about 30°. The flask was cooled with ice water if necessary. After the addition of $AlCl_3$, the ice water was removed and the stirring continued for 4-5 hours. During all this time HCl gas was given off. After allowing the flask to stand overnight its content assumed a dark reddish color and was treated with ice and hydrochloric acid. The hydrolyzed product was then extracted three times with ether and dried. The ether was removed by distillation and the residue fractionated. The first fraction collected from 175-210° was proved to be some unchanged phenol and the second fraction boiling mostly at 257-258° was collected from 210-268°. This second fraction solidified on cooling and weighed 27 g. or a 66% yield of crude product. After recrystallization several times from petroleum ether it weighed 22.3 g. or 54% yield. M.p. 94-95°, b.p. 257-258°.

The results of the five condensations are listed in Table I.

(Ia) PREPARATION OF ESTERS.

Benzoyl, benzene sulfonyl, and p-toluene sulfonyl esters of the five phenols were prepared by the pyridine method (41). A typical run is described here.

One and half cc. of benzoyl chloride was added to a mixture of 1.6 g. of tert-butyl phenol dissolved in 2 cc. of pyridine in a 220 cc. flask carrying a reflux condenser. The flask was heated with a free flame until the mixture boiled. After heating for about two hours in the hood, the flask was cooled with tap water and then filled with water. The solid was suction filtered and washed thoroughly with water until there there was no odor of pyridine. The solid was purified by recrystallization from alcohol. M.p. 81-82°.

When the ester formed was a liquid a larger run was made and the product was treated with water and then extracted with ether. The ether extract was washed with dilute hydrochloric acid to remove any pyridine. After the removal of the ether, the ester was distilled under reduced pressure.

The results are given in Table Ia.

(Ib) NITRATION OF TERT-ALKYL BENZENES.

The four tertiary alkyl benzenes nitrated were tert-butylbenzene, dimethyl n-propyl phenyl methane, dimethyl isopropyl phenyl methane and diethyl methyl phenyl methane, which were prepared from the tertiary alcohols with benzene in the presence of aluminum chloride.

Each nitration was carried out according to Malherbe's procedure (12) by treating equal weights of the hydrocarbon and fuming nitric acid (1.52) at room temperature for two hours. The product was poured into water, separated, dried, and distilled under reduced pressure.

The results are given in Table Ib.

(Ic) REDUCTION OF PARA NITRO TERT-ALKYLBENZENES.

The reduction was carried out by means of tin and concentrated hydrochloric acid. A typical run is as follows.

Thirty grams of tin were put in a 500 cc. round bottom flask fitted with an air condenser. One hundred cc. of conc. HCl was added and then 20 g. of p-nitro tert-butyl benzene. After several hours the nitro compound floating on the surface changed into a crystalline mass. This was treated with a large amount of water and made alkaline with NaOH and finally steam distilled in a 2-liter flask. The amino compound coming over with the steam was separated, dried with solid KOH and distilled under reduced pressure.

The results are given in Table Ic.

(Id) OXIDATION OF PARA NITRO TERT-ALKYL BENZENES.

The oxidation method was adapted from Malherbe (12). A typical run is as follows.

One and half grams of the nitro compound and 20 cc. of dilute nitric acid (1.20) were sealed in a Carius tube and heated up to 130° in the Carius combustion furnace. From 10-14 hours white crystals usually appeared inside the tube. Then the tube was allowed to cool down and opened. The content was poured into 400 cc. of water and the white crystals suction filtered off. The white crystals was freed from some unchanged nitro compound by washing with a little cooled ether. In each case the crystals thus obtained had a melting point, 238-240°. A mixed melting point determination with p-nitrobenzoic acid showed no depression.

(Ie) PHENOLS FROM PARA AMINO TERT-ALKYL BENZENES.

A typical diazotization is as follows. Four and half grams of p-amino tert-butylbenzene were treated with 2.5 cc. of conc. sulfuric acid in 15 cc. of water. The solid salt formed was then suspended in 300 cc. of water. After cooling it down to about 5°, 1.9 g. of sodium nitrite in 8 cc. of water was added drop by drop to the stirred suspension from a dropping funnel with a capillary tube attached to the stem. The diazotized solution was then warmed on the water bath and subjected to steam distillation. p-Tert-butyl phenol was obtained, m.p. 99-100°. A mixed melting point determination showed no depression.

The other three phenols similarly obtained were proved to be identical with those prepared from the condensations.

(II) CONDENSATIONS OF SECONDARY ALCOHOLS WITH BENZENE.

Isopropyl alcohol, sec-butyl alcohol, methyl n-propyl carbinol were obtained from Eastman Kodak Co., methyl isopropyl carbinol was prepared from a method given in Organic Syntheses (39). A typical run is as follows:

One hundred and fifty-six grams (2 moles) of benzene and 100 g. (.8 mole) of $AlCl_3$ were stirred in a three-neck 1-liter flask fitted with a mercury-sealed stirrer and a short air condenser carrying a thermometer reaching to the mixture and a bent tube for the outlet of HCl gas evolved. This outfit was placed in the hood. Then from a dropping funnel attached to one of the three necks 120 g. (2 moles) of isopropyl alcohol was added drop by drop to the stirred benzene $AlCl_3$ mixture. The inside temperature was maintained at 30° or below by regulating the rate of addition of the alcohol and by cooling the flask with ice water. HCl gas was freely given off. After all the alcohol had been added the ice water was removed and the stirring continued for 4-5 hours. Then the flask was allowed to stand overnight and the red reaction product was hydrolyzed with ice and HCl. The benzene layer was separated and the aqueous layer extracted three times with ether. The combined benzene ether extract was washed with dilute HCl, a little sodium carbonate solution and finally with water. It was dried and the ether removed by distillation. The product was fractionated several times and the fraction, b.p.152-154°, was collected as the cumene. It weighed 60 g. or 25% yield.

The results are listed in Table II.

(III) CONDENSATIONS OF TERTIARY ALCOHOLS WITH BENZENE, TOLUENE, m-XYLENE, m-CRESYL METHYL ETHER AND ANISOLE.

For the condensations of tertiary alcohols a technique similar to that used in the condensations of secondary alcohols was used. m-Xylene is a technical product from Baker with a boiling range of 137-139°; m-cresyl methyl ether and anisole were prepared by methylation of m-cresol and phenol with dimethyl sulfate in a 10% NaOH solution. A typical run follows.

Thirty-one grams (.3 mole) of diethyl methyl carbinol in a dropping funnel were dropped to a stirred mixture of 117 g. (1.5 moles) of benzene and 20 g. (.15 mole) of $AlCl_3$ in a 500 cc. three-neck flask fitted with a mercury-sealed stirrer, a dropping funnel and a short air condenser carrying a thermometer reaching to the benzene mixture and a bent tube for the outlet of HCl gas evolved. The set-up was placed in the hood. The inside temperature was kept at 30° or below by regulating the rate of addition of the alcohol and by cooling the flask with ice water. HCl gas was given off and the mixture turned dark red. After the addition of the alcohol the stirring was continued for 4-5 hours and then the flask was allowed to stand overnight. The product was transferred to a 2-liter round bottom flask and steam distilled. It was separated, extracted with ether and dried. After the removal of the ether the product was fractionated. The fraction boiling at 205-208° was collected as the diethyl methyl phenyl methane. It weighed 23 g. or 47.3% yield.

The results are listed in Table III.

The tertiary butyl derivatives of m-xylene, toluene, etc., were nitrated giving nitro compounds possessing a musk-like odor. A typical nitration is described here.

Twenty grams of tert-butyl m-xylene were added slowly drop by drop from a dropping funnel to a cooled mixture of 60 g. of fuming nitric acid (1.52) and 120 g. of fuming sulfuric acid (27% fuming) in a three-neck flask the middle neck of which was introduced a thermometer reaching to the bottom of the flask and the other two necks were fitted with a dropping funnel and an air condenser respectively. The flask was cooled by ice water and vigorously whirled by hand with each drop of the hydrocarbon. The temperature was kept at about 25°. After the hydrocarbon had been added, the flask was slowly heated on the water bath until the temperature reached up to 100°. It was maintained at 100° for 10-20 minutes until a drop of the nitrated product became solid in cold water. The flask was then cooled to room temperature and its content was poured slowly into ice water contained in a 4-liter Erlenmeyer flask. The solid mass was suction filtered and washed thoroughly with water until practically free from acid. The solid was then recrystallized from alcohol. Pale yellow needles were obtained and had a very strong musk-like odor. M.p. $110-111^{\circ}$.

The other nitro compounds similarly prepared are listed in Table IIIa.

SUMMARY.

(1) Aliphatic tertiary alcohols condensed with phenol in the presence of aluminum chloride to give good yields of p-tert.-alkyl phenols. p-Tert.-butyl, -amyl, and -hexyl phenols were prepared by this method.

The three p-tert.-hexyl phenols were new compounds, their structures were established by syntheses.

2 The benzoyl, benzene sulfonyl, and p-toluene sulfonyl esters of the five phenols were prepared.

3 (~~2~~) Aliphatic secondary and tertiary alcohols each condensed with benzene ~~(or its homologs)~~ to give the corresponding alkyl benzenes in the presence of aluminum chloride. The tertiary alcohols reacted much more readily and gave higher yields than the secondary alcohols.

A procedure was described for these condensations.

(~~3~~) Aliphatic primary alcohols do not condense with either phenol nor benzene in the presence of aluminum chloride.

Table I.

CONDENSATIONS OF TERTIARY ALCOHOLS WITH PHENOL.

	Reactants in Moles					
	Alcohol	Phenol	$AlCl_3$	Product	M.P.	Yield
Tert-butyl alcohol	.25	.25	.125	p-Tert-butyl phenol (42)	99-100°	40%
Tert-amyl alcohol	.25	.25	.125	p-Tert-amyl phenol (43)	94-95°	54%
Dimethyl n-propyl carbinol	.25	.25	.125	Dimethyl n-propyl p-hydroxyphenyl methane*	37-38°	56%
Dimethyl isopropyl carbinol	.17	.17	.085	Dimethyl isopropyl p-hydroxyphenyl methane**	105-106°	47%
Diethyl methyl carbinol	.25	.25	.125	Diethyl methyl p-hydroxyphenyl methane***	59-60°	50%

Calc. for $C_{12}H_{18}O$: C, 80.89; H, 10.11
*Found: C, 80.74; H, 10.06

**Found: C, 80.80; H, 10.00

***Found: C, 80.95; H, 10.17

Table Ia.

BENZOYL ESTERS OF PARA TERTIARY ALKYL PHENOLS.

p-Tert-butylphenol (42)	M.p.81-82°		
p-Tert-amylphenol (43)	M.p.60-61°		
Dimethyl n-propyl p-hydroxyphenylmethane*	169-171° (B.p.3mm.)	*Calc. for $C_{19}H_{22}O_2$: Found;	C, 80.80; H, 7.86 C, 80.66; H, 7.65
Dimethyl isopropyl p-hydroxyphenylmethane*	M.p.54-55°	Found:	C, 80.71; H, 7.81
Diethyl methyl p-hydroxyphenylmethane*	M.p.77-78°	Found:	C, 80.72; H, 7.79

BENZENE SULFONYL ESTERS OF PARA TERTIARY ALKYL PHENOLS.

p-Tert-butylphenol	M.p.70-71°	Calc. for $C_{16}H_{18}O_3S$: Found:	S, 11.03 S, 10.97
p-Tert-amylphenol	B.p.184-185° (3 mm.)	Calc. for $C_{17}H_{20}O_3S$: Found:	S, 10.52 S, 10.26
Dimethyl n-propyl p-hydroxyphenyl methane*	B.p.174-175° (3mm.)	*Calc. for $C_{18}H_{22}O_3S$: Found:	S, 10.06 S, 9.88
Dimethyl isopropyl p-hydroxyphenyl methane*	B.p.178-179° (3 mm.)	Found:	S, 9.91
Diethyl methyl p-hydroxyphenyl methane*	B.p.183-184° (3 mm.)	Found:	S, 9.98

p-TOLUENE SULFONYL ESTERS OF PARA TERTIARY ALKYL PHENOLS.

p-Tert-butylphenol	M.p.109-110°	Calc. for $C_{17}H_{20}O_3S$: Found:	S,10.52 S,10.44
p-Tert-amylphenol	M.p.54-55°	Calc. for $C_{18}H_{22}O_3S$: Found:	S,10.06 S, 9.93
Dimethyl n-propyl p-hydroxyphenyl methane*	B.p.194-195° (3 mm.)	*Calc. for $C_{19}H_{24}O_3S$: Found:	S, 9.64 S, 9.72
Dimethyl isopropyl p-hydroxyphenyl methane*	B.p.187-188° (3 mm.)	Found:	S, 9.57
Diethyl methyl p-hydroxyphenyl methane*	B.p.188-189° (3 mm.)	Found:	S, 9.60

Tables Ib & Ic.

PARA NITRO TERTIARY ALKYL BENZENES.

p-Nitro-tert-butylbenzene (12)	B.p.137-138° (15 mm.)	Calc. for $C_{10}H_{13}O_2N$: Found:	N,7.82 N,7.68
p-Nitrophenyl dimethyl n-propyl methane*	B.p.124-126° (3 mm.)	*Calc. for $C_{12}H_{17}O_2N$: Found:	N,6.76 N,6.81
p-Nitrophenyl dimethyl isopropyl methane*	B.p.122-124° (3 mm.)	Found:	N,6.73
p-Nitrophenyl diethyl methyl methane*	B.p.123-125° (3 mm.)	Found:	N,6.70

PARA AMINO TERTIARY ALKYL BENZENES.

p-Amino-tert-butylbenzene (12)	B.p.239-240°	Calc. for $C_{10}H_{15}N$: Found:	N,9.40 N,9.32
p-Aminophenyl dimethyl n-propyl methane*	B.p.107-109° (3 mm.)	*Calc. for $C_{12}H_{19}N$: Found:	N,7.91 N,7.78
p-Aminophenyl dimethyl isopropyl methane*	B.p.109-111° (3 mm.)	Found:	N,7.95
p-Aminophenyl diethyl methyl methane*	B.p.108-110° (3 mm.)	Found:	N,7.85

Table II.

CONDENSATIONS OF SECONDARY ALCOHOLS WITH BENZENE.

	Reactants in Moles					
	Alcohol	Benzene	$AlCl_3$	Product	B.P.	Yield
Isopropyl alcohol	2	2	.8	Cumene (44)	152-154°	25%
Sec-butyl alcohol	1	1.5	.5	Sec-butyl benzene (45)	172-174°	26%
Methyl n-propyl carbinol	.25	.5	.125	Methyl n-propyl phenylmethane (46)	191-193°	25.3%
Methyl isopropyl carbinol	.18	.54	.09	Methyl isopropyl phenylmethame (47)	189-191°	28%

Table III.

CONDENSATIONS OF TERTIARY ALCOHOLS WITH BENZENE, TOLUENE, m-XYLENE, m-CRESYL METHYL ETHER AND ANISOLE.

	Reactants in Moles					
	Alcohol	Benzene etc.	$AlCl_3$	Product	B.P.	Yield
Diethyl methyl carbinol	.3	1.5 (Benzene)	.15	Diethylmethyl phenylmethane (48)	205-208°	47.3%
Tert-butyl alcohol	.5	1 (m-Xylene)	.25	Tert-butyl m-Xylene (40)	88-89° (10 mm.)	37%
Tert-butyl alcohol	.5	1 (Toluene)	.25	Tert-butyl toluene (40)	186-191°	65%
Tert-butyl alcohol	.76	.76 (m-Cresyl methylether)	.3	Tert-butyl m-cresyl methyl ether (40)	215-230°	30%
Tert-butyl alcohol	.3	.6 (Anisole)	.15	Tert-butyl anisole (49)	220-222°	72%
Tert-amyl alcohol	.2	.6 (Anisole)	.15	Tert-amyl anisole	234-235°	52%
Diethyl methyl carbinol	.2	.6 (Anisole)	.15	Diethylmethyl methoxyphenyl methane	250-253°	70%
Dimethyl n-propyl carbinol	.3	.6 (Anisole)	.15	Dimethyl n-propyl methoxyphenyl methane	249-251°	74.5%
Dimethyl isopropyl carbinol	.2	.6 (Anisole)	.15	Dimethyl isopropyl methoxyphenyl methane	250-253°	70%

Table IIIa.

NITRO DERIVATIVES OF TERTIARY BUTYL TOLUENE, m-XYLENE, METHY m-CRESYL ETHER AND ANISOLE.

	Product	M.P.	Odor
Tert-butyl m-xylene	Trinitro-tert-butyl m-xylene (40)	110-111°	musk
Tert-butyl toluene	Trinitro-tert-butyl toluene (40)	96-97°	musk
Tert-butyl m-cresyl methyl ether	Dinitro-tert-butyl m-cresyl methyl ether (40)	85-86°	musk
Tert-butyl anisole	Dinitro-tert-butyl anisole (49)	100°	no odor
Dimethyl isopropyl methoxyphenyl methane	Dinitro-derivative (?)	62-63°	some odor

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Part II.

REARRANGEMENT OF BENZYL PHENYL ETHERS BY MEANS OF ALUMINUM CHLORIDE.

INTRODUCTION.

In connection with condensation studies in this Laboratory a benzyl phenyl ether was recently isolated from the benzylation of 2,6-dichlorophenol with benzyl alcohol in the presence of aluminum chloride (1). The main product was identified as 4-benzyl-2,6-dichlorophenol and the isolated ether was proven to be the benzyl ether of 2,6-dichlorophenol. This suggests that benzylation of phenols in general, and the chlorine substituted phenols in particular by this aluminum chloride method may take place through the intermediate formation of the ether.

Consequently a search in the literature was made to find if there were cases where benzyl phenyl ethers or alkyl phenyl ethers were ever brought into reaction with aluminum chloride. It was found that in 1892 Hartmann and Gattermann (2) had reported the action of aluminum chloride on a few alkyl phenyl ethers. In case of anisole it decomposed almost quantitatively into phenol, but when isobutyl phenyl ether was treated with aluminum chloride it gave the p-butyl phenol, indicating for the first and only time that an alkyl phenyl ether can be rearranged to a para substituted alkyl phenol by means of aluminum chloride. Norris and Young (3), Scholl and Seer (4), Frankforter and Daniels (5) also reported the action of aluminum chloride on triphenylmethyl alkyl ethers, phenol ethers and alkyl ethers, respectively. However it was not found in the literature that a benzyl phenyl ether can be rearranged to the benzyl phenol in the presence of aluminum chloride.

In 1927 Van Alphen (6) converted benzyl phenyl ether into p-benzyl phenol by means of zinc chloride. Two years later Short and Stewart (7) also reported the benzyl phenyl ether rearrangement by means of zinc chloride or HCl. Inasmuch as zinc chloride and aluminum chloride act alike in certain organic reactions such as the Friedel and Crafts reaction, it was decided to try the action of aluminum chloride on benzyl phenyl ether to see if there would be any reaction.

Therefore a run was made by treating benzyl phenyl ether with aluminum chloride and a reaction was noticed when the mixture was heated on an oil bath to above 100° for a few hours. After the usual work-up, p-benzyl phenol was isolated and identified. Besides the benzyl phenol, there were also formed some phenol and a high boiling mixture. Subsequently, benzyl 2,6-dichlorophenyl ether was treated with aluminum chloride from which the p-benzyl 2,6-dichlorophenol was isolated and identified.

These preliminary experimental facts thus obtained substantiate the suggestion that condensations of phenols with benzyl alcohol in the presence of aluminum chloride may take place through the intermediate formation of the benzyl ether.

Other benzyl phenyl or cresyl ethers also react with aluminum chloride to give substituted benzyl phenols or cresols.

REVIEW OF LITERATURE.

In 1828 Wohler (8) reported the classical experiment of changing ammonium cyanate into urea which represents the first observed case of molecular rearrangement as well as the first synthesis of an organic compound from inorganic sources. Since then there are numerous cases of molecular rearrangement. The subject of ether rearrangement or decomposition by heat has been comprehensively reviewed by Hurd (9). Porter (10) also has briefly described the rearrangement of ethers. Within the last few years a quite number of studies on ether rearrangement have been reported in the different periodicals. Therefore only a brief sketch is outlined here.

In 1883 Sichilone (11) reported that the allyl ether of salicylic ester when heated and subsequently hydrolyzed with KOH gave a mixture of allyl substituted salicylic acids. Later Claisen (12) proved that the mixture consists of allyl and propenyl salicylic acids.

In 1887 Claisen (12) reported that heat alone can convert allyl phenyl ethers into allyl phenols. Since then many similar rearrangement has been reported in the literature.

In 1906 Bucherer and Grobe (13) reported the case of concentrated sulfuric acid to change a phenol ether into a substituted phenol.

In 1914 Kursanov investigated some ether rearrangement by means of HCl (14).

The use of zinc chloride or HCl to rearrange benzyl phenyl ether has been reported by Van Alphen (6), and Short and Stewart (7).

Shorigin (15) since 1924 has used metallic sodium for the rearrangement of ethers.

Since 1931 Niederl and co-workers (16) have used a mixture of sulfuric acid and glacial acetic acid to rearrange alkyl phenyl ethers.

The use of boron fluoride to rearrange alkyl phenyl ethers has been discovered by Nieuwland and his students (17).

Roger Adams (18) in 1920 showed that benzyl phenyl ether can not be rearranged by heat. However in 1934 the rearrangement of benzyl phenyl ethers at high temperatures has been reported by Behaghel and Freiensehner (19).

In 1933 Smith (20) discovered that tertiary alkyl phenyl ethers can be rearranged to the p-tert-alkyl phenols by heat. He also reported the rearrangement of some alkyl phenyl ethers by means of aluminum chloride discovered by Hartmann and Gattermann (2).

EXPERIMENTAL.

I. Benzyl phenyl ether and $AlCl_3$:

(a) Fifty-two grams (.3 mole) of benzyl phenyl ether and 20 g. (.15 mole) of $AlCl_3$ were mixed in a 500 cc. flask fitted with a reflux condenser. The flask was then heated on an oil bath and a vigorous reaction took place when the temperature of the oil bath reached about 100°. HCl gas was freely given off. After heated for six and half hours at a temperature of 140-160°, the heavy and tarry reaction product was treated with water and extracted three times with ether. The ether extract was dried and the ether removed by distillation. The residue was distilled under reduced pressure. The first fraction, b.p. 70-110° (2-3 mm.), weighed 9 g. and later it was proved to be phenol. The second fraction, b.p. 145-160° (2 mm.), weighed 15 g. and crystallized immediately after being seeded with a crystal of p-benzyl phenol. It was purified by recrystallization from petroleum ether, m.p. 84°. A mixed melting point determination with known p-benzyl phenol showed no depression. No definite product was isolated from the higher boiling fraction.

(b) This second run was made by using the same amount of material except that the ether and $AlCl_3$ were mixed in 150 cc. of petroleum ether. The mixture was allowed to react at room temperature. There was no sign of reaction within the first 10-15 minutes but after that a vigorous boilin of the petroleum ether was noticed and HCl gas was freely given off.

The flask was then immersed in cooled water until the boiling of the petroleum ether had subsided. After three days a heavy dark colored oil settled down at the bottom of the flask. This was hydrolyzed, extracted with ether, dried and distilled. The first fraction, b.p. 70-110° (3 mm.), weighed 8 g. and was identified as phenol. The second fraction, b.p. 140-180° (3 mm.), weighed 16 g. and then treated with ligroin. After this ligroin solution was heated to boiling, a heavy oil separated and was identified as the o-benzyl phenol by its mono-bromo derivative. From the mother ligroin liquer pure p-benzyl phenol was deposited on cooling, m.p. 84°. The amount of o- and p-benzyl phenols thus separated was about the same. The o-benzyl phenol when brominated in chloroform solution gave a bromine derivative, m.p. 55-56°. This bromine derivative was proved by mixed melting point determination to be identical with one obtained from the bromination of o-benzyl phenol prepared by the Claisen reaction. Benzylation of p-bromophenol with benzyl alcohol in the presence of aluminum chloride also gave the same bromo derivative. The higher boiling fraction gave no definite compound.

II. Benzyl 2,6-dichlorophenyl ether and $AlCl_3$:

One hundred cc. of petroleum ether in a 500 cc. round bottom flask was treated with 25.6 g. (.1 mole) of benzyl 2,6-dichlorophenyl ether and 7 g. (.05 mole) of $AlCl_3$. After three days a dark reddish oil settled down at the bottom of the flask. This was worked out in the usual manner. One fraction, b.p.180-185° (4 mm.), weighed 10 g. and was purified by recrystallization from petroleum ether, m.p. 59-60°. It was identified as p-benzyl 2,6-dichlorophenol by a mixed melting point determination. There was obtained also some five grams of unchanged ether.

III. Benzyl 2,4-dichlorophenyl ether and $AlCl_3$:

This experiment was carried out in the same manner as the previous one. One hundred cc. of petroleum ether, 50.6 g. (.2 mole) of benzyl 2,4-dichlorophenyl ether and 27 g. (.2 mole) of $AlCl_3$ were used. After three days and the usual work-up, a fraction, b.p. 150-185° (5 mm.), weighed 21 g. and solidified. It was recrystallized from high test gasoline, m.p. 79-80°. A mixed melting point determination with 2,4-dichloro-6-benzyl phenol showed no depression. A few grams of unchanged ether was also obtained. No attempt was made to purify the heavy high boiling mixture.

IV. Benzyl p-chlorophenyl ether and $AlCl_3$:

Twenty-two grams (.1 mole) of the benzyl ether, 7 g. (.05 mole) of $AlCl_3$ and 75 cc. of petroleum ether were used in this experiment. After three days the product was worked up in the usual way. One fraction, b.p. 140-175° (5 mm.), was seeded with a crystal of 2-benzyl 4-chlorophenol and it solidified. After recrystallization it weighed 4.5 g., m.p. 47-48°. It was proved to be 2-benzyl 4-chlorophenol by mixed melting point determination. No definite compound was obtained from the higher boiling mixture.

V. Benzyl p-cresyl ether and $AlCl_3$:

This experiment was carried out similarly as the benzyl phenyl ethers. Eighty cc. of petroleum ether, 19.8 g. (.1 mole) of benzyl p-cresyl ether and 7 g. (.05 mole) of $AlCl_3$ were used. After three days the reaction product was worked up in the customary manner. A fraction, b.p. 120-155° (5 mm.), solidified on cooling. It was recrystallized from petroleum ether, m.p. 35-36°. A mono-bromo derivative prepared by bromination in chloroform solution melted at 46-48° after being recrystallized from petroleum ether. This mono-bromine derivative was proved to be identical with one obtained by bromination of 2-benzyl p-cresol in chloroform as reported by Huston (21) in the melting point.

SUMMARY.

Benzyl phenyl ethers reacted with aluminum chloride to give small yields of rearranged products--the benzyl phenols.

These experiments substantiate the suggestion that benzylation of phenols with benzyl alcohol by the aluminum chloride method may take place through the intermediate formation of the benzyl ether.

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