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Studies in the diphenyl series : IV. ethers and esters of para- and ortho- hydroxy diphenyl.

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STUDIES IN THE DIPHENYL SERIES

IV. ETHERS AND ESTERS OF PARA- AND ORTHO- HYDROXY DIPHENYL

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By

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INTRODUCTION

A study of the literature reveals that diphenyl and its derivatives have always held great possibilities for research work. The chief characteristic of the parent compound is that it consists of two benzene rings directly united, or in other words, a hydrogen atom of benzene is replaced by a phenyl group. Theoretically, each hydrogen of the two nuclei might be replaced by various other groups, and thus form a series of derivatives similar to those of benzene. For example phenol C_6H_5OH resembles hydroxy diphenyl $C_6H_5C_6H_4OH$, although of course there are three isomers of the latter compound.

The discovery of diphenyl by Fittig in 1862, opened this new field in Organic Chemistry. His method of synthesis consisted of allowing sodium or copper bronze to react on an ethereal solution of monoiodo-benzene (1).

$$2\ C_6H_5I + 2\ Cu \longrightarrow C_6H_5.C_6H_5 + Cu_2I_2.$$

Further impetus was given to the chemistry of diphenyl when Berthelot, in 1866, discovered a new method. He found that when benzene was passed through a red hot tube it decomposed chiefly into hydrogen and diphenyl (2). If benzene can change so readily into diphenyl, it would be surprising if diphenyl would

not continue to undergo pyrolysis in this manner. It has been found that diphenyl does decompose at elevated temperatures into 4,4'-diphenylbiphenyl (3).

It seems that benzidine (4), nitro-diphenyls (5), and amino diphenyls (6) have held the interest of the research chemist, and more work has been accomplished with these than with any other derivatives of diphenyl. Hinkle and Hey (7), however, worked extensively on halogenated diphenyls. In 1874, Osten (8) prepared acetamidodiphenyl and amidodiphenyl, producing the latter by the action of potassium nitrite and sulphuric acid on monohydroxy diphenyl. Schultz, whose name is oftenest linked with the study of diphenyl and its derivatives, worked on bromo- and nitrodiphenyls (9).

Hydroxy diphenyl was chosen for this study because it is now available in commercial quantities, and there are several derivatives which are not known, as well as a large amount of theoretical material. Hydroxy diphenyls may be obtained from the diphenyl derivatives by methods similar to those by which the phenols are prepared from the benzene derivatives. Hydroxy diphenyls have been prepared in good yields by the following methods:

1. Diazotization of 4-amino diphenyl (10).
2. Warming one part of potassium salt of diphenyl sulphonic acid and three parts of potassium hydroxide (11).
3. Oxidation of phenols with caustic potash (12).

Practically all of the hydroxy diphenyl which is commercially available is secured as a by-product from the hydrolysis of chlorobenzene under pressure (13). It constitutes one of the main ingredients of the waste tar left after phenol and diphenyl oxide have been removed from the reaction mass. This tar contains 20-25 per cent of mono-hydroxy diphenyl compounds, of which at least three-fourths is para-hydroxy diphenyl. Ortho- and para-hydroxy diphenyl may be separated by fractionally hydrolyzing a mixture of the alkali metal salts of these compounds in aqueous solutions, such as by heating with aqueous hydrochloric acid at 85°. The solid para-phenyl phenol is removed at the end of each successive hydrolytic step before repeating a similar fractionation (14).

Apparently there is a marked difference between the ortho- and para-hydroxy diphenyls. For

example, the sodium salt of para-hydroxy diphenyl is very difficult to prepare. It must be crystallized from 10 per cent sodium hydroxide using 20 per cent excess of the solution, over the theoretical amount. The sodium salt of ortho-hydroxy diphenyl may be prepared by neutralizing with dilute sodium hydroxide, and evaporating the resulting solution to dryness. Para-hydroxy diphenyl has no appreciable odor, while ortho-hydroxy diphenyl has the characteristic phenolic odor. The Kolbe synthesis did not go to completion with para-hydroxy diphenyl, while a 30 per cent yield was secured from the ortho compound. Ortho-hydroxy diphenyl responds to all the chemical reactions for a phenol, with the exception of the red color formation with ferric chloride, giving here a green color. The change in color might be due to the presence of the diphenyl radical.

Since little specific work has been done on the reactivity of hydroxy diphenyls, the reactivity and general properties of phenols and cresols were reviewed, in order that they might throw some light on the problem. Hydroxy diphenyl may be compared to phenol and more especially to cresol, when one considers the fact that a methyl group of cresol is

replaced by a phenyl group in hydroxy diphenyl.

It was found that phenols and cresols are readily hydrogenated at higher pressures; hydrogenation of phenols was easier than that of cresols. The reaction velocity of the above cresols was meta greater than para and para greater than ortho (15). The stability of cresols is as follows: the meta greater than the ortho and the ortho greater than the para, whereas the stability of dichlorophenol derivatives decreases with an increase in molecular weight (16). The rate of reaction of acetyl bromide with a phenol in a non-ionizing solvent increases with the acidity of the phenol; the slow reaction of the ortho derivatives of bromo- and chloro-phenols may be ascribed to steric hindrance. The para-derivatives react more rapidly than the meta derivatives (17). It is a well known fact that the position of the substituents on a benzene ring directly affects their reactivity toward substitution reactions. This is shown in the case of the cresols where the meta derivative is more reactive than the para, which in turn is more reactive than the ortho (18). In the decomposition of phenol and naphthol ethers

by means of concentrated hydrochloric acid, results show that the meta derivatives decompose the least and the para the most (19). In this study it was possible to work with para- and ortho- hydroxy diphenyls, as they were the only ones available.

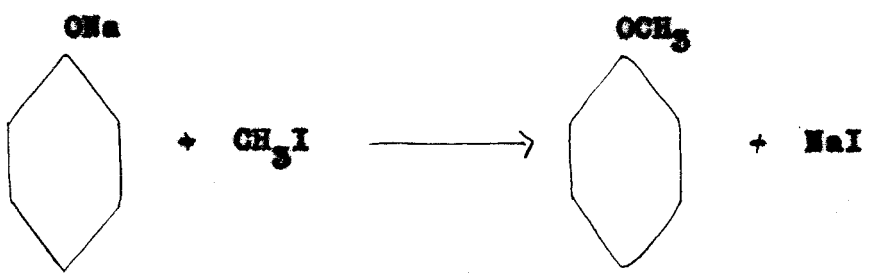
THEORETICAL

The specific problem here attacked is first, the possibility of preparing the ethers and esters of ortho and para hydroxy diphenyl by the action of alkyl and aryl halides upon the sodium salt, without the aid of catalysts, and second, if successful in their preparation, to study rearrangements in this series.

Williamson (20) in 1851 prepared ethers by the following reaction:

$$C_2H_5ONa + C_3H_7I \longrightarrow C_2H_5.O.C_3H_7 + NaI$$

This synthesis enables one to prepare a simple or a mixed ether, either aliphatic or aromatic. Anisole for example, may be prepared thus:



Since anisole may be prepared by the above method, it is only reasonable to expect that the sodium salt of hydroxy diphenyl, when treated with an alkyl halide, should also yield the corresponding ether.

Torley and Matter (21)(22) prepared the

phenyl ether by the action of alkali alcoholates or phenates upon halogenated aromatic hydrocarbons at 320°, in the presence of copper as a catalyst.

$$C_6H_5C_6H_4ONa + C_6H_5Cl = C_6H_5C_6H_4.O.C_6H_5 + NaCl \quad (21)$$

$$C_6H_5C_6H_4ONa + C_6H_5C_6H_4Cl = C_6H_5C_6H_4.O.C_6H_4C_6H_5 + NaCl \quad (22)$$

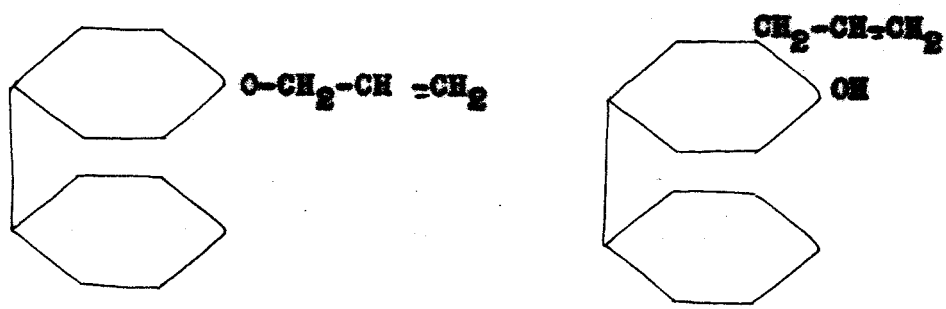
Esters may also be prepared by the action of an acyl halide on an alcohol or alcoholate. In many cases the use of the latter is preferable because the sodium chloride does not cause hydrolysis, while hydrochloric acid may.

$$C_2H_5ONa + CH_3COCl = CH_3.COOC_2H_5 + NaCl$$

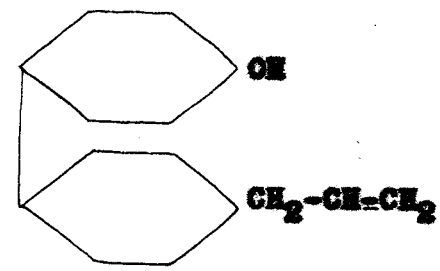
It is of interest in this connection to note that Otto Hönigschmid in 1901 (23), prepared ortho hydroxy diphenylacetate from ortho hydroxy diphenyl and sodium acetate with acetic anhydride.

In the study of hydroxy diphenyl, it must be borne in mind that rearrangement may occur. However rearrangement has not been observed in this study. Ortho substituted compounds rearrange more rapidly than their meta or para isomers. In the pyrolysis of the allyl ether of hydroxy diphenyl, the usual ortho rearrangement takes place rather than the

formation of the p'-isomer (24).



and not

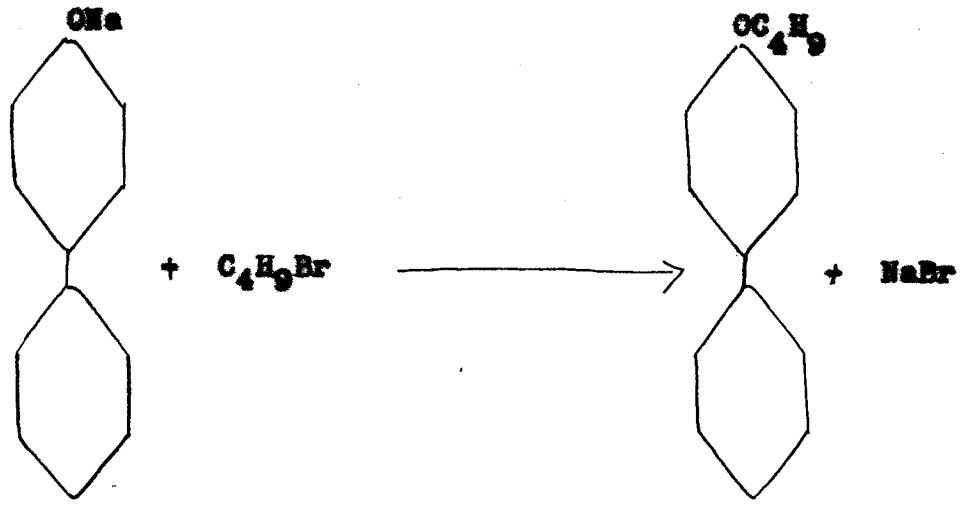


The Kaufler formula, which was used by the investigators in the above study, is not now considered correct.

The foregoing discussion makes obvious the great possibilities for experimentation which hydroxydiphenyl offers to the research chemist. The compounds which were prepared in this particular study, were analyzed for carbon and hydrogen by Liebig's combustion method (25).

EXPERIMENTAL

REACTION BETWEEN THE SODIUM SALT OF PARA-HYDROXY DIPHENYL AND BUTYL BROMIDE



A mixture of 19.2 grams (0.1 mol) of the sodium salt of para hydroxy diphenyl and 39.87 grams (0.3 mol) of butyl bromide was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 101°, for 9 hours. No reaction took place when butyl bromide was added to the sodium salt of para hydroxy diphenyl. After 9 hours the reaction product was brought to the boiling point and filtered. The precipitate, which was thought to be sodium bromide, was washed with dry ether to remove all traces of organic matter. The weight of the precipitate was 15.5 grams, corresponding to 51.1 per cent of the theoretical. The filtrate was distilled to remove the excess butyl bromide. The residue in the distilling flask was a liquid.

The flask while hot was submerged in a beaker of water and crystals formed. The product was recrystallized from hot glacial acetic acid, with a melting point of 73°. The yield was 0.2 gram, corresponding to 0.88 per cent of the theoretical.

In a second run the same molar quantities were used. In order to determine whether time was a governing factor, the reaction mixture was allowed to reflux for 43 hours. At the end of this time the reaction mixture was treated as previously described. The precipitate this time weighed 8.5 grams, corresponding to 27 per cent of the theoretical, showing that the first precipitate contained some unchanged sodium salt of para hydroxy diphenyl. The crystals from the filtrate when dried, weighed 11.4 grams. The product recrystallized from hot glacial acetic acid, formed flaky, white crystals, with a melting point of 71°. The yield was 5.7 grams, corresponding to 25 per cent of the theoretical.

In a third run the same molar quantities were used. However, the sodium salt of para hydroxy-diphenyl was carefully dried and the butyl bromide redistilled. The reaction mixture was allowed to reflux 25 hours. When treated as before, the precipitate weighed 11 grams, corresponding to 35

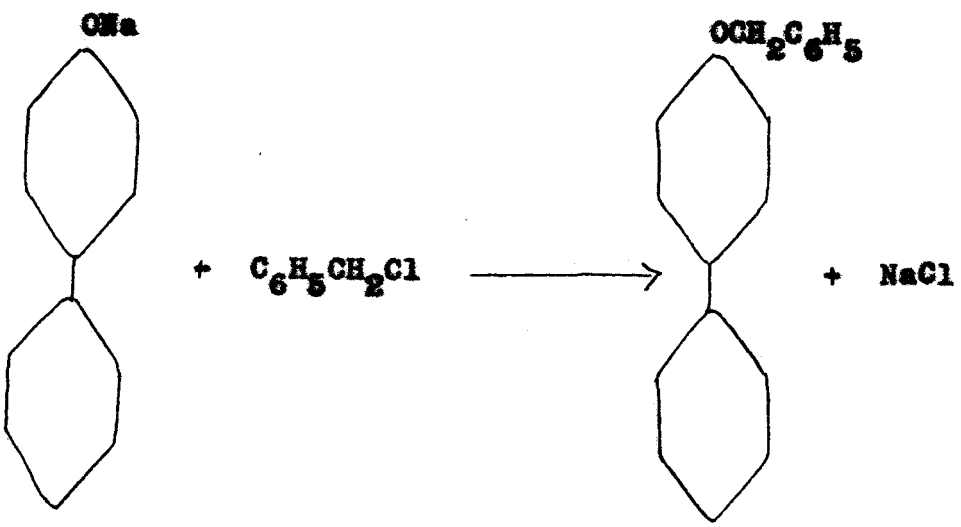
per cent of the theoretical, and the crystals from the filtrate weighed 4 grams. This product recrystallized from hot glacial acetic acid, had a melting point of 72°. The yield was 2.4 grams, corresponding to 10.6 per cent of the theoretical.

Analysis: Calculated for Butyl Diphenyl Ether

C. 84.9 % H. 7.96 %

Found C. 82.3 % H. 7.87 %

REACTION BETWEEN THE SODIUM SALT OF PARA-HYDROXY DIPHENYL AND BENZYL CHLORIDE



A mixture of 19.2 grams (0,1 mol) of the sodium salt of para hydroxy diphenyl and 37.8 grams (0.3 mol) of benzyl chloride was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 176-179°, for 6.5 hours. After refluxing, the reaction mixture was filtered while

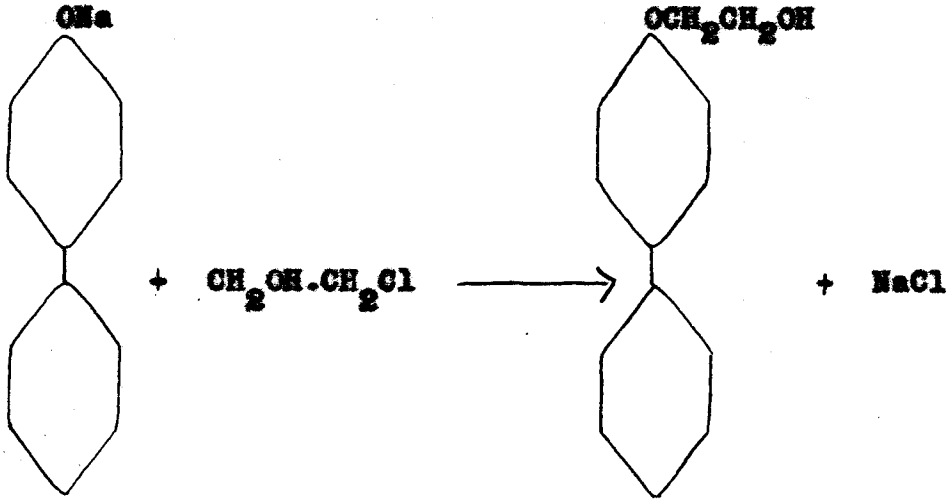
hot. The filtrate was comprised of two immiscible liquids. The bottom layer was colorless, while the top layer was a reddish-brown. Crystals formed in this reddish-brown layer, on cooling. The crystals when dried, weighed 7.2 grams and had a melting point of 128°. The product when recrystallized from hot glacial acetic acid, melted at 130°. The yield was 2.6 grams, corresponding to 7.18 per cent of the theoretical. When the colorless layer, previously mentioned, was distilled it formed crystals; the solid when dissolved in water and tested with silver nitrate gave a positive chloride test, showing that sodium chloride the theoretical end-product of the reaction was formed.

In a second run the same molar quantities were used. However, the sodium salt of para hydroxy-diphenyl was carefully dried and the benzyl chloride redistilled. The reaction mixture was allowed to reflux for 15 hours. When filtered hot at the end of this time, the filtrate crystallized completely. The product when dried, weighed 7 grams. When re-crystallized from hot glacial acetic acid, the compound had a melting point of 131°. The yield was 2.3 grams, corresponding to 6.07 per cent of the theoretical.

Analysis: Calculated for Benzyl Diphenyl Ether

	C. 87.6 %	H. 6.15 %
Found	C. 84.4 %	H. 5.98 %

REACTION BETWEEN THE SODIUM SALT OF PARA-HYDROXY DIPHENYL AND ETHYLENE CHLORHYDRIN



A mixture of 19.2 grams (0.1 mol) of the sodium salt of para hydroxy diphenyl and 32.2 grams (0.4 mol) of ethylene chlorhydrin was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 128°, for 30 hours. No reaction was noticeable when ethylene chlorhydrin was added to the sodium salt of para hydroxy diphenyl. After 30 hours the reaction mixture was filtered, while still hot, and the precipitate weighed 5.4 grams. Crystals formed in the filtrate, which when dried, weighed 13.8 grams. The product was re-crystallized from hot toluene, and had a melting point of 106°. The solid was inclined to be some-

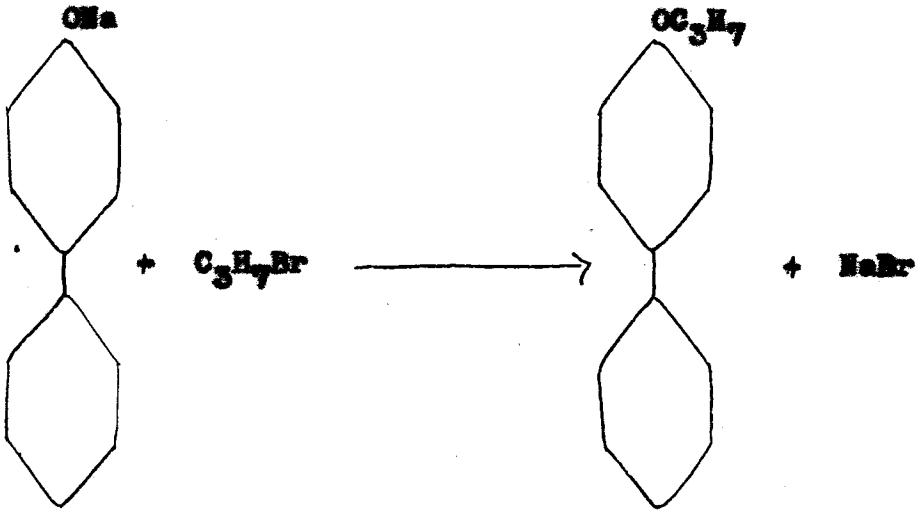
what powdery in form.. The yield was 4.6 grams, corresponding to 23.7 per cent of the theoretical.

Analysis: Calculated for Beta chloro ethyl Diphenyl Ether

C. 78.4 % H. 6.54 %

Found C. 70.9 % H. 5.06 %

REACTION BETWEEN THE SODIUM SALT OF PARA-HYDROXY DIPHENYL AND PROPYL BROMIDE



A mixture of 19.2 grams (0.1 mol) of the sodium salt of para hydroxy diphenyl and 36.9 grams (0.3 mol) of normal propyl bromide was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 71.5°, for 64 hours. No reaction took place when normal propyl bromide was first added to the sodium salt of para hydroxy-diphenyl. After refluxing for 2.5 hours, a solid white cake formed. In order to keep the reaction mixture liquid, 36.9 grams (0.3 mol) of normal

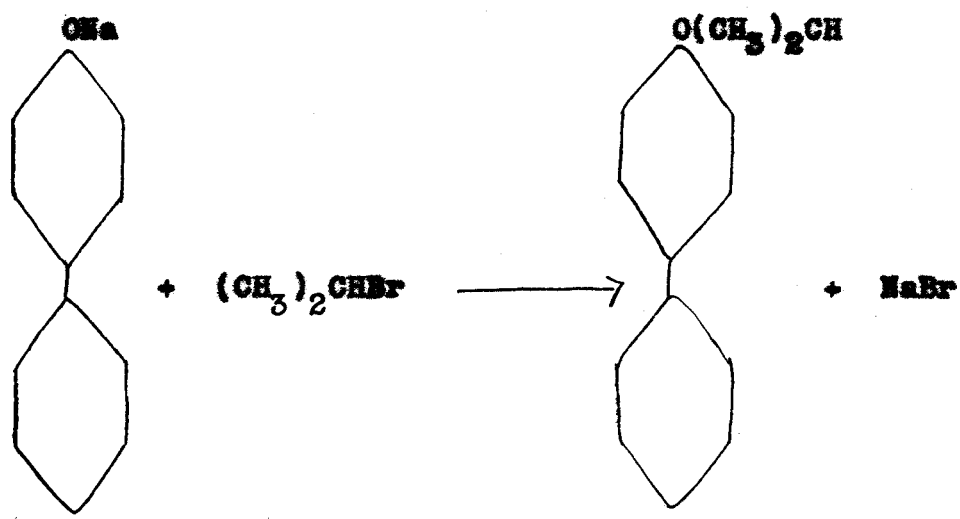
propyl bromide was added. The mixture was then allowed to reflux for 64 hours. At the end of this time the reaction mixture was filtered, while hot. The precipitate weighed 13 grams. Since no crystals formed on cooling the filtrate, the excess propyl bromide was distilled off and the remaining liquid was placed in an ice and salt bath. Crystals formed which weighed 3.1 grams. The product recrystallized from hot alcohol in white, flaky crystals, having a melting point of 71°. The final yield was 1.5 grams, corresponding to 7.8 per cent of the theoretical.

Analysis: Calculated for Propyl Diphenyl Ether

C. 84.4 % H. 7.54 %

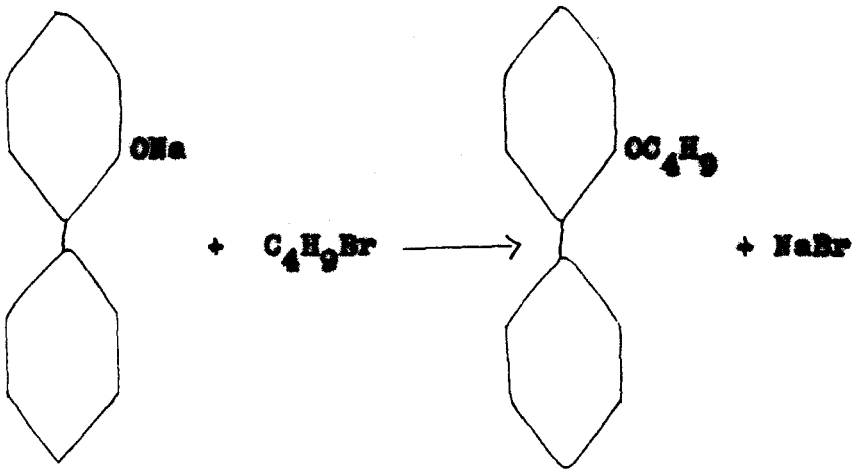
Found C. 78.2 % H. 5.87 %

REACTION BETWEEN THE SODIUM SALT OF PARA-HYDROXY DIPHENYL AND ISO-PROPYL BROMIDE



A mixture of 19.2 grams (0.1 mol) of the sodium salt of para hydroxy diphenyl and 36.4 grams (0.3 mol) of iso-propyl bromide was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 59-60°, for 15 hours. An excess of 36.4 grams (0.3 mol) of iso-propyl bromide was added to the reaction mixture after 2 hours refluxing; during practically all of the time a solid mass remained. After 15 hours the white cake was removed from the flask and purified by recrystallization from hot glacial acetic acid. The melting point of the compound was 153°. A mixture of this compound and known para hydroxy diphenyl melted exactly at 162°; therefore the compound was unchanged para hydroxy diphenyl. The yield was 8.5 grams, corresponding to 50 per cent of the theoretical.

REACTION BETWEEN THE SODIUM SALT OF ORTHO-HYDROXY DIPHENYL AND BUTYL BROMIDE



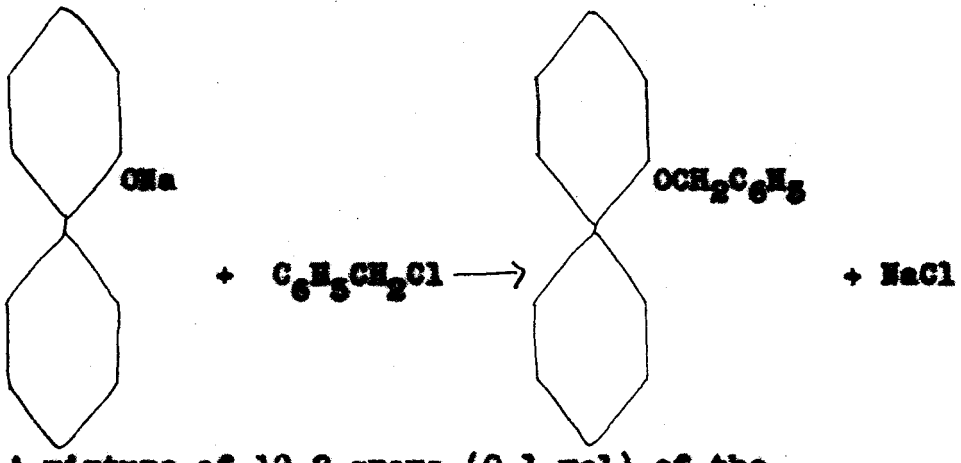
A mixture of 19.2 grams (0.1 mol) of the sodium salt of ortho hydroxy diphenyl and 39.8 grams (0.3 mol) of butyl bromide was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 101°, for 9 hours. No reaction was noticeable when the butyl bromide was first added to the ortho salt. At the end of this time the reaction product was brought to the boiling point and filtered. The precipitate amounted to 2.8 grams. The filtrate was of an orange color and entirely liquid. When vacuum distilled, the filtrate yielded the following fractions:

	Temperature	Pressure	Color
# 1	125°	730 mm.	light orange
# 2	130°	730 mm.	light orange

In a second run the same molar quantities were used. The reaction mixture was allowed to reflux for 35 hours. When purified as before there was but a small amount of precipitate. The crystals weighed 1.8 grams. The filtrate which was a reddish, oily liquid, when vacuum distilled yielded the following fractions:

	Temperature	Pressure	Color
# 1	127°	730 mm.	light color (yellow)
# 2	132°	730 mm.	light color (yellow)

REACTION BETWEEN THE SODIUM SALT OF ORTHO-HYDROXY DIPHENYL AND BENZYL CHLORIDE



A mixture of 19.2 grams (0.1 mol) of the sodium salt of ortho hydroxy diphenyl and 37.8 grams (0.3 mol) of benzyl chloride was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 176-179°, for 6.5 hours. No reaction was noticeable when benzyl chloride was first added to the ortho salt. The reaction when heated

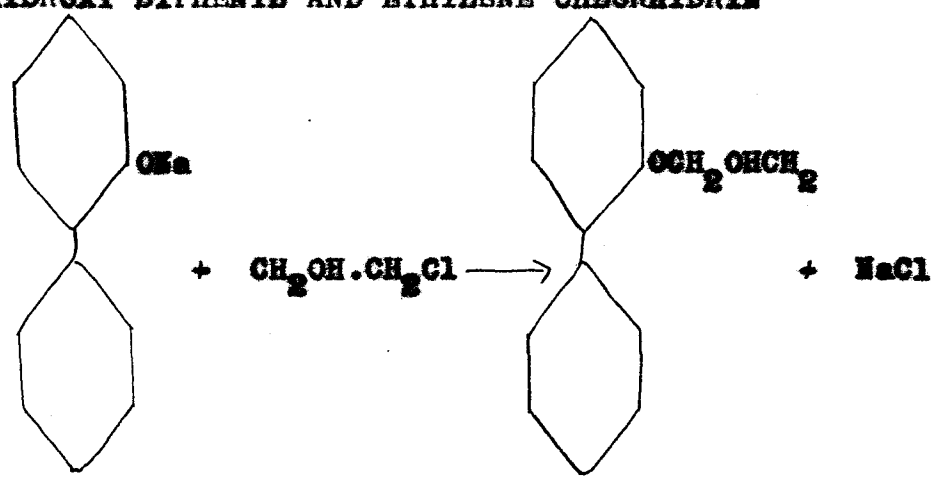
went from a red, to a green, to a lemon, to an orange color which persisted to the end. The filtrate was a cloudy, red color, which when vacuum distilled, gave the following fractions:

	Temperature	Pressure	Color
# 1	99-100°	730 mm.	colorless
# 2	142-144°	730 mm.	colorless
# 3	185°	730 mm.	crystals (M.P.55°)
# 4	200°	730 mm.	very dark red

In a second run the same molar quantities were used. However, the ortho salt was carefully dried and the benzyl chloride redistilled. The reaction mixture was allowed to reflux for 15 hours. When treated as previously described, the filtrate was a cloudy, orange color, which when vacuum distilled yielded the following fractions:

	Temperature	Pressure	Color
# 1	90-100°	710 mm.	colorless
# 2	175°	710 mm.	lightyellow
# 3	150-171°	710 mm.	lemon
# 4	189°	710 mm.	deep orange

REACTION BETWEEN THE SODIUM SALT OF ORTHO-HYDROXY DIPHENYL AND ETHYLENE CHLORHYDRIN

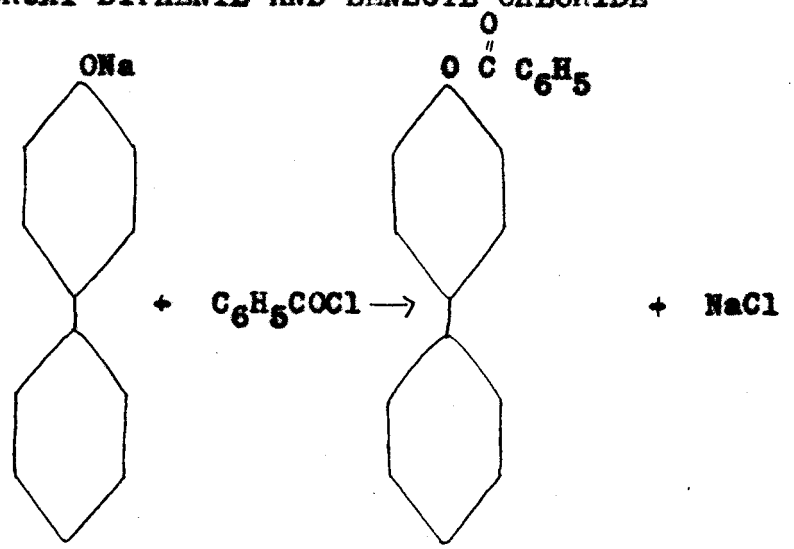


A mixture of 19.2 grams (0.1 mol) of the sodium salt of ortho hydroxy diphenyl and 32.2 grams (0.4 mol) of ethylene chlorhydrin was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 128°, for 30 hours. No reaction was noticeable when ethylene chlorhydrin was added to the ortho salt. After 30 hours, the reaction mixture was brought to the boiling point and filtered, the precipitate weighed 4 grams. The filtrate which was a very dark liquid, when vacuum distilled yielded the following fractions:

	Temperature	Pressure	Color
# 1	98-120°	730 mm.	colorless
# 2	130-153°	730 mm.	yellow

A study of the reactions between brom-benzene and the ortho and para sodium salt of hydroxy diphenyl, as well as propyl and iso-propyl bromides upon the sodium salt of ortho hydroxy diphenyl was made, but time did not permit an analysis of the products which were formed.

REACTION BETWEEN THE SODIUM SALT OF PARA-HYDROXY DIPHENYL AND BENZOYL CHLORIDE

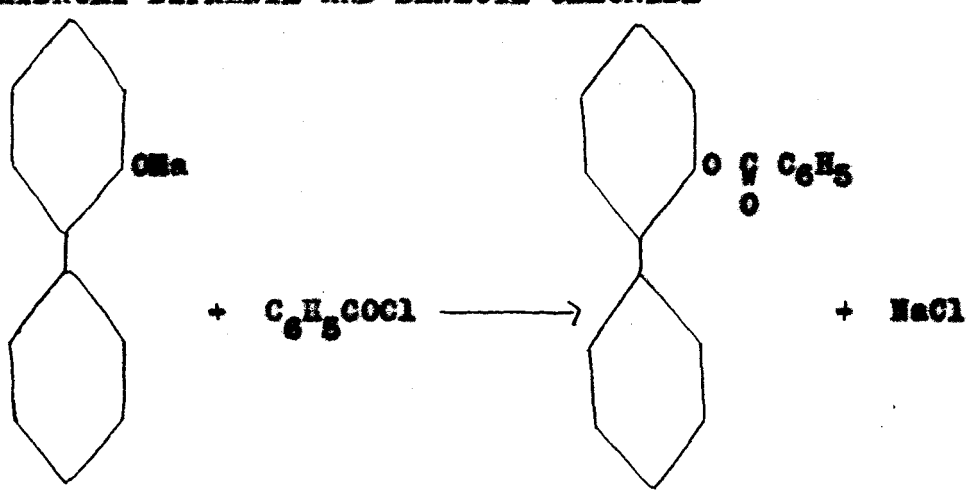


A mixture of 19.2 grams (0.1 mol) of the sodium salt of para hydroxy diphenyl and 56.2 grams (0.4 mol) of benzoyl chloride was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 198°, for 5 hours. A violent reaction took place when benzoyl chloride was added to the para salt. After refluxing for 5 hours, a huge, white cake formed in the flask, that partially dissolved in hot water, yielding benzoic acid. The residue was treated eight times with hot water and the benzoic acid removed, which amounted to 32.8 grams, corresponding to 67 per cent of the theoretical. The residue was recrystallized from hot glacial acetic acid. It had a melting point of 148°. The melting point of this product as found in the literature was 150° (26).

The yield was 12.5 grams, corresponding to 45 per cent of the theoretical.

In a second run the same molar quantities were used. The sodium salt was carefully dried and the benzoyl chloride redistilled. The reaction product was allowed to reflux for 3 hours. A violent reaction took place when benzoyl chloride was added to the sodium salt. When treated as previously described benzoic acid formed to the extent of 14.7 grams, corresponding to 30 per cent of the theoretical. The residue was recrystallized from hot glacial acetic acid. Its melting point was 145-146°. The product was then recrystallized from hot toluene and its melting point raised to 148°. The yield was 8.5 grams, corresponding to 31 per cent of the theoretical.

REACTION BETWEEN THE SODIUM SALT OF ORTHO-HYDROXY DIPHENYL AND BENZOYL CHLORIDE

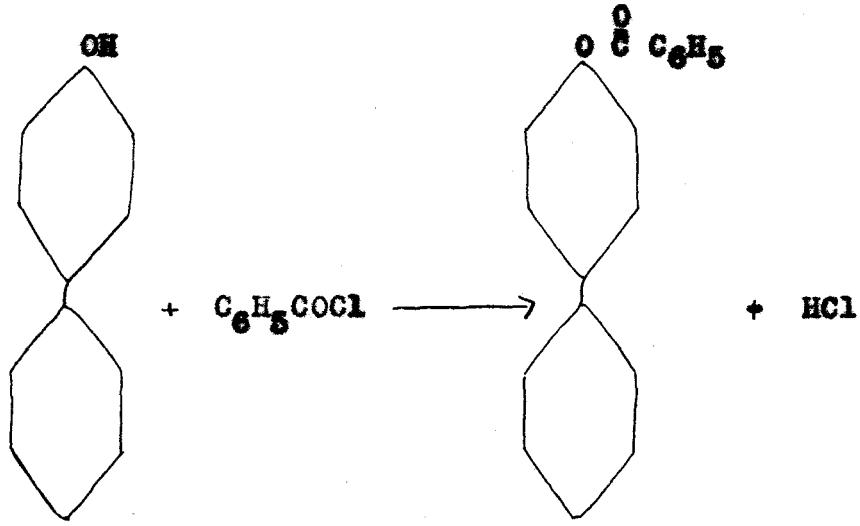


A mixture of 19.2 grams (0.1 mol) of the sodium salt of ortho hydroxy diphenyl and 56.2 grams (0.4 mol) of benzoyl chloride was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 198°, for 3 hours. A violent reaction took place when benzoyl chloride was added to the ortho salt. After refluxing for 3 hours, a large pink cake formed, which partly dissolved in hot water, yielding benzoic acid. The residue was redissolved 6 times in hot water and the benzoic acid removed, which amounted to 16.7 grams, corresponding to 34 per cent of the theoretical. The product left was recrystallized from hot alcohol. Its melting point was 58-59°. The yield was 21.8 grams, corresponding to 58 per cent of the theoretical.

In a second run the same molar quantities were used. The sodium salt of ortho hydroxy diphenyl was carefully dried and the benzoyl chloride redistilled. The reaction mixture was allowed to reflux for 3.5 hours. When treated as previously described, benzoic acid formed to the extent of 20.3 grams, corresponding to 43 per cent of the theoretical. The residue was recrystallized from hot alcohol. Its melting point was 59°.. The yield was 12 grams, corresponding to 43 per cent of

the theoretical.

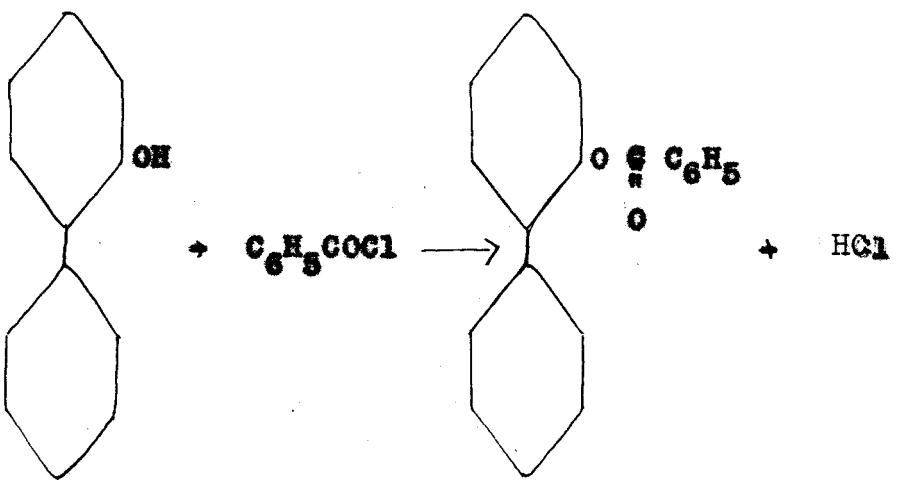
REACTION BETWEEN PARA-HYDROXY DIPHENYL AND BENZOYL CHLORIDE



A mixture of 17 grams (0.1 mol) of para-hydroxy diphenyl and 68 grams (0.4 mol) of benzoyl chloride was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 198°, for 11 hours. There was no noticeable reaction when benzoyl chloride was added to the para-hydroxy diphenyl. After a few minutes of heating the reaction mixture became a cherry red liquid; after heating for several hours, it became black. After refluxing for 11 hours the reaction mixture was brought to the boiling point and filtered. The excess benzoyl chloride was destroyed in hot water and benzoic acid formed to the extent of 17 grams,

which corresponds to 24.3 per cent of the theoretical. The residue was recrystallized from hot toluene, and the compound had a melting point of 144°. The yield was 11 grams, corresponding to 40 per cent of the theoretical.

REACTION BETWEEN ORTHO-HYDROXY DIPHENYL AND BENZOYL CHLORIDE



A mixture of 17 grams (0.1 mol) of ortho-hydroxy diphenyl and 68 grams (0.4 mol) of benzoyl chloride was heated in a 200 c.c. round bottom flask connected to a reflux condenser, at a temperature of 198°, for 8 hours. There was no reaction when benzoyl chloride was added to the ortho hydroxy-diphenyl. Practically all of the compound dissolved, forming a dark, lemon colored solution. After one hour of heating this reaction mixture turned black. The hydrochloric acid which was given off was

collected in a beaker of water and tested with litmus paper. When the reaction was completed, the reaction mixture was filtered. No precipitate formed on cooling. About 100 c.c. of 10 per cent sodium hydroxide was added to the filtrate, which was well shaken and then filtered. The filtrate was then treated with hydrochloric acid and sodium benzoate formed. After removing the sodium benzoate, the reaction mass was treated several times with hot water to remove the benzoic acid, which amounted to 4 grams. The reaction product was then treated with hot alcohol, the crystals had a melting point of 62°. The yield was 9 grams, corresponding to 32.9 per cent of the theoretical.

SUMMARY

The Williamson reaction has been applied to the sodium salts of ortho and para hydroxy diphenyls using various alkyl and aryl halides. It has been observed that the reaction was quite slow, and the yields were much lower than was expected. A peculiar difference between the products secured from para hydroxy diphenyl and those secured from ortho hydroxy diphenyl was that while the former were solids, as was expected, the latter were liquids, which was not expected. While these products were probably ethers, the analyses of them has not proved this definitely. Possibly the products were slightly impure, although the solids ones had a definite sharp, melting point, which repeated recrystallization did not raise. Further study along this line is projected for the immediate future.

Application of a similar reaction, using instead of aryl and alkyl halides, acyl halides gave products which were believed to be esters, and in every case solids were produced. The analyses of them, have not yet proved that they are esters. Possibly the products were slightly impure, although each one had a definite, sharp, melting point, which repeated recrystallization did not raise. Further study along this line is projected for the immediate future.

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