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Unsaturated Phenyl Ethers and their Rearrangements
UNSATURATED PHENYL ETHERS AND THEIR REARRANGEMENTS

BY

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I.

INTRODUCTION

Claisen has shown that the allyl phenyl ethers readily rearrange at their boiling points into the isomeric o-allyl phenols:

\[
\begin{align*}
\text{OH} & \quad \text{C}_3\text{H}_5 \\
\text{H} & \quad \text{O} \quad \text{C}_3\text{H}_5 \\
\end{align*}
\]

This investigation was undertaken in order to determine whether or not other unsaturated phenyl ethers would undergo a similar rearrangement. The ethers chosen for study in this work were those with an \( \alpha\beta \) or \( \gamma\delta \) ethylene linkage (C=C), those with \( \beta\gamma \)-acetylenic (C≡C) or cyan (C≡N) linkages, and the benzyl ethers.

This thesis deals with the preparation of certain ethers of the types mentioned above, and with the effect of heat upon these ethers.
In his work on the O- and O-alkyl derivatives of acetoacetic ester, Claisen observed a marked difference between the saturated O-alkyl ethers and the O-allyl ethers. Whereas, the saturated radicals, as methyl, ethyl, etc., showed no tendency to wander from the oxygen to the carbon, the allyl radical readily shifted its position in the molecule:

\[
\begin{align*}
\text{CH}_3-C=CH-COOC_2H_5 \quad & \text{Stable} \\
\text{OCH}_3 \\
\end{align*}
\]

but

\[
\begin{align*}
\text{CH}_3-C=CH-COOC_2H_5 \quad & \xrightarrow{\text{heat}} \quad \text{CH}_3-C=CH-COOC_2H_5 \\
\text{OC}_3H_5 & \quad \text{O C}_3H_5 \\
\end{align*}
\]

A similar wandering of the allyl group was found to take place in the case of O-allyl acetylacetone:

\[
\begin{align*}
\text{CH}_3-C=CH-C=CH_3 \quad & \xrightarrow{\text{heat}} \quad \text{CH}_3-C=CH-C=CH_3 \\
\text{OC}_3H_5 & \quad \text{O C}_3H_5 \\
\end{align*}
\]

Claisen (loc. cit.) then investigated the allyl ethers of \(\beta\)-naphthol and guaiacol and found that on heating them to 210° to 230° C they rearranged to the isomeric allyl phenols:

The first case of such a rearrangement developed in an investigation by Scichilone of the allyl ether of salicylic acid. He prepared the allyl ether of methyl salicylate from allyl iodide and the sodium salt of methyl salicylate and purified his product.
by distillation at atmospheric pressure. On hydrolysis, he obtained an acid which analyzed for the allyl ether of salicylic acid. However, this acid gave an intense violet color with ferric chloride, a reaction which is not given by any other known ether of salicylic acid.

This anomalous behavior was not explained until Claisen prepared the allyl ether of ethyl salicylate and showed that by heating it to 230° for one hour, he could convert it completely into the ethyl ester of C-allyl salicylic acid:

\[
\begin{align*}
\text{H} & \quad \text{OC}_3\text{H}_5 \\
\text{COOC}_2\text{H}_5 & \quad \rightarrow \\
\text{C}_3\text{H}_5 & \quad \text{OH} \\
\text{COOC}_2\text{H}_5
\end{align*}
\]

This ester gave on hydrolysis the same acid which Scichilone had obtained, thus indicating that Scichilone's acid was not the allyl ether of salicylic acid, as he thought, but was C-allyl salicylic acid:

\[
\begin{align*}
\text{C}_3\text{H}_5 & \quad \text{OH} \\
\text{COOH}
\end{align*}
\]

The formation of this acid can readily be explained in the light of Claisen's work. The allyl ether of the methyl ester, which Scichilone obtained as the initial product of the reaction between allyl iodide and the sodium salt of methyl salicylate, had rearranged into the C-allyl derivative on distillation at atmospheric pressure. This on hydrolysis gave the hydroxy-acid, which gave with ferric chloride the normal reaction for phenolic hydroxyl.

Claisen then investigated the allyl ethers of a great number of substituted phenols, such as p-chloro phenol, p-bromo phenol, p-oxyazobenzene, p-oxybenzaldehyde, and a host of others; and found
that without exception they underwent this rearrangement when heated to boiling for some time. Some years later he applied the same reaction to the allyl ethers of the nitroso- and amino-phenols.

He found that in the rearrangement the allyl groups took a position ortho to the hydroxyl if possible. If, however, both ortho positions were occupied, the allyl group entered the para position, if that were unoccupied:

\[
\begin{align*}
\text{HOC}_3\text{H}_5 & \quad \text{C}_3\text{H}_5 \quad \text{OH} \\
\text{X} & \quad \text{X} & \quad \text{X}
\end{align*}
\]

The resulting allyl phenols could of course be converted into their allyl ethers and Claisen found that these also rearranged, this introducing a second allyl group into the ring:

\[
\begin{align*}
\text{HOC}_3\text{H}_5 & \quad \text{C}_3\text{H}_5 \\
\text{OH} & \quad \text{X}
\end{align*}
\]

He further established that a third allyl group could be introduced under certain conditions. If the para position was open, the third allyl group entered in that place. Furthermore, if the para position or either of the ortho positions was occupied by -COOH or -CHO, the rearrangement took place with elimination of the -COOH or -CHO as CO₂ or CO respectively:

\[
\begin{align*}
\text{HOOC}_3\text{H}_5 & \quad \text{X} \\
\text{OH} & \quad \text{X}
\end{align*}
\]

He then applied the reaction to more complex substances and succeeded in synthesizing a number of naturally occurring allyl and propenyl compounds, such as eugenol, o-eugenol, esdragol, anol and other important constituents of essential oils.
Since the discovery of this reaction, several other investigators have made use of it in synthetical work. Thus Auwers and Borsche prepared 3,5-dimethyl-2-allyl phenol from the allyl ether of m-5-xylenol,

\[
\begin{align*}
\text{OC}_3\text{H}_5 \quad &\rightarrow \quad \text{H} \\
\text{CH}_3 &\rightarrow \quad \text{CH}_3 \\
\end{align*}
\]

Jacobs and Heidelberger, and later Adams and Rindfusz, prepared o-allyl phenol by heating allyl phenyl ether,

\[
\begin{align*}
\text{OC}_3\text{H}_5 \quad &\rightarrow \quad \text{OH} \\
\text{H} &\rightarrow \quad \text{C}_3\text{H}_5 \\
\end{align*}
\]

Mauthner prepared 4-allyl-2,5-dimethoxy-phenol from the corresponding ether,

\[
\begin{align*}
\text{OC}_3\text{H}_5 \quad &\rightarrow \quad \text{OH} \\
\text{CH}_3 \text{O} \quad &\rightarrow \quad \text{CH}_3 \text{O} \\
\end{align*}
\]

This he converted into the methyl ether which he changed into the isomeric propenyl compound. This on treatment with ozone and hydrolysis of the resulting ozonide yielded gallaaldehyde trimethyl ether,

\[
\begin{align*}
\text{CH}_3 \text{O} \quad &\rightarrow \quad \text{CH}_3 \text{O} \\
\text{CH}_2\text{CH}=\text{CH}_2 &\rightarrow \quad \text{CH}_2\text{CH}=\text{CH}_2 \\
\end{align*}
\]

Furthermore, Claisen showed that the o-allyl phenols could be converted into cyclic ethers by heating them with pyridin hydrobro-
The formation of cyclic ethers from the α-allyl phenols was also investigated by Adams and Rindfusz (loc. cit.), who showed that the acetyl α-allyl phenol dibromides yielded unsaturated cyclic ethers on treatment with alcoholic potassium hydroxide,

It is thus evident that this reaction is of great importance in synthetic organic chemistry. It furnishes a beautiful method for the preparation of α-allyl-phenols, of α-propenyl phenols by rearrangement of the α-allyl phenols, and of α-oxy-(alkoxy) aldehydes by oxidation of the propenyl phenols (or their alkyl ethers). Further, it gives us a convenient method for the preparation of various coumaran derivatives, as indicated by Claisen, and by Adams and Rindfusz.

In view of the importance and wide scope of this reaction, it was thought worth while to investigate the behaviour of other unsaturated phenyl ethers, such as phenyl propargyl ether, phenyl butenyl ether and others.

The present investigation deals with the phenyl ethers with αβ or γδ ethylene linkages, and those with acetylenic and CN linkages. It also includes a study of the phenyl benzyl ethers.
It has long been known that the allyl group differs markedly from the saturated alkyl groups. The allyl group appears to be characterized by a very loose attachment to the halogens, to nitrogen, and to oxygen.

Clark has found that the rate of the reaction between allyl bromide and pyridin in absolute alcohol solution is approximately seventy times that of n-propyl bromide. He found for allyl bromide, $K = 1.353$, and for n-propyl bromide, $K = .0179$, where $K$ is the reaction velocity constant for the bimolecular reaction:

$$RBr + C_6H_5N \rightarrow C_6H_5N<Br$$

Collie and Schryver showed that trimethylallylammonium chloride decomposed upon distillation with the formation of allyl chloride and trimethylamine, indicating that the allyl group is attached to the nitrogen less firmly than the methyl,

$$(\text{CH}_3)_3C_3H_5N\cdot Cl \xrightarrow{\Delta} (\text{CH}_3)_3N + C_3H_5Cl$$

They found the same to be true in the case of the corresponding hydroxide

$$(\text{CH}_3)_3C_3H_5N\cdot OH \xrightarrow{\Delta} (\text{CH}_3)_3N + C_3H_5OH$$

Komatsu found that in the decomposition of the substituted phenylammonium hydroxides,

$$C_6H_5\cdot NXY(C_3H_5)OH,$$

where $X$ and $Y$ were methyl or ethyl, the allyl was eliminated.
v. Braun, who has made an exhaustive study of the decomposition of the quaternary ammonium compounds gives the following as the order in which the groups are eliminated from the ammonium salts:

\[ C_3H_5; C_6H_5CH_2; CH_3; C_2H_5; C_3H_7; \text{etc.} \]

And for decomposition of the ammonium hydroxides, he gives the following:

\[ C_3H_5; C_6H_5CH_2; C_2H_5; C_3H_7; i-C_5H_{11}; \text{etc.} \]

It will be noticed that the allyl group is eliminated far more readily than the corresponding saturated group n-propyl.

A very similar behaviour is found in the decomposition of the cyanogen bromide addition compounds of tertiary amines. v. Braun has shown that in general the smallest group is eliminated as the bromide,

\[ \text{CH}_3(C_6H_5)(C_3H_7)N\stackrel{\text{CN}}{\text{Br}} \rightarrow \text{CH}_3\text{Br} + C_2H_5(C_3H_7)N\cdot\text{CN} \]

On the other hand, if an allyl group is present, it is eliminated as allyl bromide,

\[ C_6H_5(CH_3)(C_3H_5)N\stackrel{\text{CN}}{\text{Br}} \rightarrow C_3H_5\text{Br} + C_6H_5(CH_3)N\cdot\text{CN} \]

The greater reactivity of the allyl bromide is explained by Clark (loc. cit.) as being due to the presence of the unsaturated groups \(-C=O\). In the group \(-CH_2\cdot CH=CH_2\), the residual valence of the unsaturated group seems to strengthen the union between it and the methylene group. This tends to diminish the residual valence of the methylene group, thus loosening its attachment to the halogen.

This strengthening of the union between the unsaturated group
-C=\text{-} and any group united to it, accounts for the subnormal reactivity of vinyl iodide, \( \text{CH}_2=\text{CH-I} \). The low reactivity of the aryl halides may possibly be due to the same effect.

In view of this subnormal reactivity of vinyl iodide, it was expected that phenyl vinyl ether would not rearrange. This was found to be the case.

v. Braun has also established that in the decomposition of unsaturated quaternary ammonium hydroxides of the type,

\[
\text{CH}_2=\text{CH-(CH}_2)_x\text{NOH}
\]

the tendency for the unsaturated radical to be eliminated as a diolefine is far greater than that of the corresponding saturated compound. On the other hand, this difference decreases as the double bond is shifted farther away from the nitrogen. Thus n-hexyl trimethylammonium hydroxide, \( \text{C}_6\text{H}_13\text{N(CH}_3)_3\text{OH} \) breaks down to give 73\% hexyldimethylamin and only 27\% hexene. On the other hand hexenyl trimethylammonium hydroxide gives the diolefine almost exclusively, while decenyltrimethylammonium hydroxide

\[
\text{CH}_2=\text{CH’(CH}_2)\text{N(CH}_3)_3\text{OH}
\]

gives but 35\% of the diolefine, no more than the corresponding saturated compound.

In view of these facts, it was thought that, if the decomposition of the quaternary ammonium compounds, and the rearrangement of the phenyl ethers are dependent upon the same principles, butenyl phenyl ether, \( \text{CH}_2=\text{CH-CH}_2\text{’CH}_2\text{’O’C}_6\text{H}_5 \) should rearrange to the isomeric butenyl phenol, but slower than the allyl. However, neither butenyl phenyl ether, pentenylphenyl ether nor hexenylphenyl ether underwent rearrangement. All three are very stable towards heat
even at 280°.

That the reactivity of the group, as measured by the method of Clark (loc. cit.) or by that of v. Braun, is not the sole determining factor in the rearrangement of the allyl ethers is further established by the behaviour of the benzyl and cyanomethyl ethers. According to Clark, $K$ for allyl bromide is 1.253 and that for benzyl bromide is 5.118. According to this, the benzyl phenyl ethers should rearrange approximately four times as readily as the corresponding allyl ethers. However, no evidence of any such rearrangement was obtained in the case of the benzyl phenyl ethers.

On the other hand, high reactivity of the group does not necessarily have to lead to rearrangement. The benzyl group may be easily split off from the oxygen, with the formation of phenol. Phenol in considerable quantity was actually found among the decomposition products of benzyl phenyl ether. Toluene was also produced, also indicating a scission of the molecule between the oxygen and the benzyl group.

Among the so called "negative groups", the cyan group, $-\text{C}≡\text{N}$, is one of the most effective. If the reactivity of the group influences the rearrangement, phenoxy acetonitril, $\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 - \text{C}≡\text{N}$, should rearrange easily. This was not the case however, nor did decomposition with the formation of phenol take place readily.

Phenylpropargyl ether, $\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 - \text{C≡CH}$, which resembles phenylallyl ether very closely, was found to be very unstable. Heat decomposed it almost completely, with the formation of heavy
tars, consequently no direct evidence is available in regard to this rearrangement.

It has thus been established that under the influence of heat alone, the following types of phenyl ethers do not rearrange to the isomeric phenols:

\[
\begin{align*}
&\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} &= \text{CR}_2 \\
&\text{C}_6\text{H}_5\text{O} \cdot \text{CH} &= \text{CH}_2 \\
&\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{C} &= \text{CH} \\
&\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{C} &= \text{EN} \\
&\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5
\end{align*}
\]

It would appear that, either this reaction is peculiar to the allyl phenyl ethers, or that an ethylene linkage to the oxygen atom is necessary. The determination of this point forms part of another investigation.
EXPERIMENTAL

The phenyl ethers used in this investigation were for the most part prepared by the published methods. In some cases, however, the methods have been modified and improved. For ethers which are not described in the literature, methods of synthesis were devised.

The attempts to rearrange the ethers were carried out by heating the ethers to their boiling points for some time. If this led to much decomposition, the ether was dissolved in a lower boiling solvent, such as di-isoamyl ether or diethylaniline, and heated for a longer time.

Constancy of the boiling point was taken as sufficient evidence that no rearrangement had taken place. Whenever a rise in temperature indicated the possibility of a rearrangement having taken place, a test for alkali soluble material was made. The absence of any such alkali soluble material, other than the original phenol, was usually taken as sufficient evidence that no rearrangement had taken place.
4-Phenoxybutene

This ether was prepared by the method of v. Braun, as follows:

Trimethylene bromide and sodium phenolate react in absolute alcoholic solution to give 3-phenoxypropyl bromide, which is converted by treatment with sodium cyanide into -phenoxybutyronitrile:

$$\text{C}_6\text{H}_5\cdot\text{ONa} + \text{Br}(\text{CH}_2)_3\text{Br} \rightarrow \text{C}_6\text{H}_5\cdot\text{O}(\text{CH}_2)_3\text{Br} + \text{NaBr}$$

$$\text{C}_6\text{H}_5\cdot\text{O}(\text{CH}_2)_3\text{Br} + \text{NaCN} \rightarrow \text{C}_6\text{H}_5\text{O}(\text{CH}_2)_3\cdot\text{CN} + \text{NaBr}$$

The $\gamma$-phenoxybutyronitrile on reduction with sodium and alcohol by Ladenburg's method yields 4-phenoxybutylamin, which by exhaustive methylation yields the desired 4-phenoxybutene:

$$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_3\text{CN} \xrightarrow{(\text{Na})/(\text{C}_2\text{H}_5\text{OH})} \text{C}_6\text{H}_5\text{O}(\text{CH}_2)_4\text{NH}_2$$

$$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_4\text{NH}_2 \xrightarrow{\text{CH}_3\text{I}/\text{Ag}_2\text{O}} \text{C}_6\text{H}_5\text{O}\cdot(\text{CH}_2)_4\text{N}(\text{CH}_3)\text{OH}$$

$$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_4\text{N}(\text{CH}_3)\text{OH} \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2 + (\text{CH}_3)_3\text{N} + \text{H}_2\text{O}$$

3-Phenoxypropyl Bromide

$$\text{C}_6\text{H}_5\text{O}\cdot(\text{CH}_2)_3\text{Br}$$

Twenty-three grams of sodium (1 atom) were dissolved in 800 cc. of absolute alcohol; to this solution were added 94 grams of phenol (1 mol) and 404 grams trimethylene bromide (2 mols) and the mixture was refluxed for ten hours. At the end of this time most of the alcohol was distilled off, the residue diluted with water and the oily layer taken up in ether. The ether solution was washed with dilute alkali, then with water, and dried over sodium sulfate. After removal of the ether the residual oil was fract-
ionated under diminished pressure, collecting the fraction distilling from 140° to 155° (at 25 mm.), which was sufficiently pure. 3-Phenoxypropyl bromide is a colorless heavy liquid boiling at 149° at 25 mm., Yield 140 grams or 65% of the theoretical. From the lower boiling fraction the excess trimethylene bromide was recovered and used again.

**γ-Phenoxybutyronitril**  \( \text{C}_6\text{H}_5\text{O} \cdot (\text{CH}_2)_3\text{CN} \)

To a solution of 150 grams phenoxypropyl bromide in 1 liter of 95% alcohol was added a solution of 115 grams sodium cyanide in 300 cc. water, and the mixture heated on the water bath for 15 hours. At the end of this time the alcohol was distilled off, the residue diluted with water and the oily layer taken up in ether. The ether solution was washed with water and dried over sodium sulfate. After removal of the ether, the residue was fractionated under diminished pressure, collecting the fraction distilling between 160° and 190° at 50 mm. The nitril forms a colorless liquid with a peculiar persistent odor. It boils at 164-6° at 50 mm., and 285° to 290° at atmospheric pressure. Yield 60 grams or 73% of the theoretical.

**4-Phenoxybutylamine Hydrochloride**  \( \text{C}_6\text{H}_5\text{O} \cdot (\text{CH}_2)_4\text{NH}_2 \cdot \text{HCl} \)

One hundred grams γ-phenoxybutyronitril were dissolved in 2.5 liters absolute alcohol and 200 grams sodium were added in portions of 10 to 20 grams. After the addition of all the sodium the mixture was allowed to cool and then distilled with steam until most of the alcohol had been driven over. The residue was then diluted
with water and the upper layer of amine and unchanged nitril taken up in ether. From this solution the amine was extracted by treatment with dilute HCl. The acid solution was then evaporated to dryness, leaving the phenoxybutylamine hydrochloride as a light brown crystalline mass. Yield 90 grams or 72% of the theoretical. The free amine was obtained from the hydrochloride by treatment with strong sodium hydroxide solution and subsequent extraction with ether.

4-Phenoxybutyl-trimethylammonium iodide \[ C_6H_5O(CH_2)_4N(CH_3)_3I \]

Seventy grams 4-phenoxybutylamine were dissolved in 1000 cc. methyl alcohol, a solution of 75 grams NaOH in 200 cc. water added, and then 216 grams methyl iodide added cautiously. It was found that if the methyl iodide was added all at once, the reaction was so violent that a large portion of the methyl iodide which had not yet reacted was projected violently from the top of the condenser. After all of the methyl iodide had been added, the mixture was refluxed for 8 hours on the water bath. The mixture was allowed to cool, when the quaternary ammonium iodide separated out in shiny flakes. These were filtered off and washed with a little cold alcohol, M. P. 165°.

4-Phenoxybutene \[ C_6H_5O·CH_2CH_2CH=CH_2 \]

Sixty-seven grams 4-phenoxybutyl-trimethylammonium iodide (0.2 mol) were suspended in 300 cc. of water and treated with an excess of silver oxide, shaking well to insure complete reaction. The solution of 4-phenoxybutyl-trimethylammonium hydroxide was
filtered from the silver iodide and evaporated almost to dryness on the water bath. The oily residue was then distilled from a small distilling flask, using a free flame. The start of the decomposition was marked by the evolution of trimethylamine. The distillate, consisting of 4-phenoxybutene, 4-phenoxybutyldimethylamine and some dissolved trimethylamine, was taken up in ether and the ether solution washed with dilute hydrochloric acid to remove the free amines, and dried over sodium sulphate. The ether was then removed and the residue fractionated, yielding a colorless liquid with a very pronounced odor resembling that of allyl phenyl ether. B. P. 209°.

As the decomposition of the quaternary ammonium hydroxide goes 43% to the formation of 4-phenoxybutene and 55% to the formation of 4-phenoxybutyldimethylamine (v. Braun, loc. cit.), the hydrochloric acid solution obtained above was made alkaline and extracted with ether. After removal of the ether the 4-phenoxybutyldimethylamine remained as a brown oil, which on treatment with methyl iodide regenerated the 4-phenoxybutyltrimethylammonium iodide. This, of course, was treated in the same manner as before.

Attempts to Rearrange 4-Phenoxybutene

1. Twenty grams of 4-phenoxybutene were heated to boiling under a reflux for 48 hours. It boiled constantly at 209° throughout the entire time. At the end of this time the contents of the flask were dissolved in ether and washed twice with 10% potassium hydroxide solution. The alkaline solution gave no pre-
cipitate when acidified with dilute sulphuric acid, indicating that no phenol was present. From the ether solution the 4-phenoxy-butene was recovered.

2. Twenty grams 4-phenoxybutene were heated in a sealed tube to 250° to 270° for five hours. The ether was recovered unchanged.

5-Phenoxy-2-Pentene

\[\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}=\text{CH} \cdot \text{CH}_3\]

Solonina prepared this ether by the action of an excess of alcoholic sodium phenolate upon 1,4-dibromopentane,

\[2\text{C}_6\text{H}_5\text{ONa} + \text{CH}_2\text{BrCH}_2\text{CH}_2\text{CHBrCH}_3 \rightarrow \text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2\text{CH}=\text{CH} \cdot \text{CH}_3 + \text{C}_6\text{H}_5\text{OH} + 2\text{NaBr}\]

On account of the difficulty of obtaining 1,4-dibromopentane, the following method was used in preparing the phenoxypentane used in this research:

Sodium acetoacetic ester and \(\omega\)-bromophenetole give \(\beta\)-phenoxy-ethylacetoacetic ester, which is hydrolyzed to \(\gamma\)-phenoxypropyl methyl ketone,

\[\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br} + \text{CH}_3\text{COCHNa} \cdot \text{COOC}_2\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2\text{CH}=\text{CH} \cdot \text{CH}_3 + \text{NaBr}\]

\[\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2\text{CH}=\text{CH} \cdot \text{CH}_3 \text{COOC}_2\text{H}_5 \text{hydrolysis} \rightarrow \text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2\text{CH}_2\cdot \text{CH}_2\cdot \text{CO} \cdot \text{CH}_3\]

The ketone on reduction gives the secondary alcohol, which is then converted into the corresponding bromide.
\[
C_6H_5O\cdot(CH_2)_3CO\cdotCH_3 + 2H \rightarrow C_6H_5O\cdot(CH_2)_3CHOH\cdotCH_3
\]

\[
3C_6H_5O\cdot(CH_2)_3\cdotCHOH\cdotCH_3 + PBr_3 \rightarrow 3C_6H_5O\cdot(CH_3)_3CHBr\cdotCH_3 + P(OH)_3
\]

This bromide, on treatment with alcoholic potassium hydroxide, gives the desired phenoxypropene,

\[
C_6H_5O\cdot(CH_2)_3\cdotCHBr\cdotCH_3 + KOH \rightarrow C_6H_5O(CH_2)_2CH=CH-CH_3 + KBr + H_2O
\]

ω-Bromophenolone \( C_6H_5O\cdotCH_2CH_2Br \)

The ω-Bromophenolone was prepared by the method of Wohl and Berthold with slight modification. 660 grams (3.5 mols) ethylene dibromide, 280 grams (3 mols) phenol, and 1000 cc. water were heated to boiling in a 5 liter flask fitted with an upright condenser. Then 500 cc. of 4N NaOH solution (2 mols) were added in portions of 25 cc. every half-hour. After the last of the NaOH had been added, the mixture was heated two hours longer. After cooling, the lower oily layer was separated from the upper aqueous layer, washed with dilute sodium hydroxide solution, and distilled. It was found convenient to distill off the excess ethylene dibromide under atmospheric pressure and then to fractionate the residue under diminished pressure, collecting the fraction boiling between 130° and 145° at 25 mm., which was practically pure -bromophenolone. It solidified on cooling to a mass of white crystals, M. P. 33°. Yield 225 grams or 55% of the theoretical.

β-Phenoxyethylacetoacetic Ester \( C_6H_5O(CH_2)_2CH<COCH_3 \)

Twenty-three grams sodium (1 atom) were dissolved in 500 cc. absolute alcohol and this solution treated with 195 (1.5 mol) acetoacetic ester. Then 202 grams -bromophenolone were immediately addi-
ed and the mixture refluxed for five hours. Most of the alcohol was then distilled off, the residue diluted with water and the oily layer taken up in ether. The ether solution was dried over sodium sulphate, the ether distilled off on the water bath and the residue fractionated under diminished pressure. Two fractions were collected, (1) all up to 160° at 22 mm., consisting mostly of excess acetoacetic ester and unchanged 2-bromophenetole, (2) from 180° to 215° at 22 mm., the product sought. This was used for the preparation of the ketone without further purification. The pure ester, obtained by repeated fractionation, boils at 205-206° at 26 mm., and forms a colorless rather viscous liquid with $n_B^o = 1.5025$. Yield 125 grams or 50% of the theoretical.

**γ-Phenoxypropyl Methyl Ketone**

One hundred grams 2-phenoxymethylacetoacetic ester and 400 cc. 10% NaOH solution were refluxed for six hours. The entire reaction mixture was then steam distilled, when the ketone came over as a pure white solid, slightly heavier than the water. This was filtered off, dried on a porous place and recrystallized from dry ether, from which it separates as large plates, M. P. 54.5°. Valentine (loc. cit.) gives the melting point as 49°. This is easily explained by the fact that he purified his product by distillation only.

By treating an ether solution of the ketone with a saturated solution of NaHSO₃, the addition compound was obtained as fine white flakes, very difficultly soluble in water.
I. \(0.6410\) gram subst. gave \(0.1630\) gram \(\text{Na}_2\text{SO}_4\)  
II. \(0.5730\) gram subst. gave \(0.1454\) gram \(\text{Na}_2\text{SO}_4\)  
Calc. for \(\text{C}_{11}\text{H}_{15}\text{O}_7\text{SNa}\) Na, 8.16; found Na, I 8.12, II 8.11  

5-Phenoxy-2-Hydroxy-n-Pentane \(\text{C}_8\text{H}_5\text{O}\cdot(\text{CH}_2)_3\text{CHOH}\cdot\text{CH}_3\)  

A suspension of 250 grams sodium bicarbonate in 1000 cc. water was covered with a solution of 36 grams -phenoxypropyl methyl ketone in 300 cc. ether and the whole cooled with ice. Then 60 grams sodium were added in small portions through a period of 36 hours, keeping the mixture cold. When all of the sodium had been used up, the ether layer was separated, washed with a saturated solution of sodium bisulfite to remove any unreduced ketone, and dried over sodium sulphate. The ether was then distilled off on the waterbath and the residue fractionated under diminished pressure, collecting the fraction distilling between 160° and 165° at 20 mm. On redistillation this gave a colorless viscous oil boiling at 163° at 20 mm. and with \(n_D^{25} = 1.5123\) and \(D_2^{25} = 1.025\).  
I. \(0.3132\) gm. subst. gave \(0.8376\) gm. \(\text{CO}_2\) and \(0.2672\) gm. \(\text{H}_2\text{O}\)  
II. \(0.2832\) gm. subst. gave \(0.7560\) gm. \(\text{CO}_2\) and \(0.2276\) gm. \(\text{H}_2\text{O}\)  
Calc. for \(\text{C}_{11}\text{H}_{16}\text{O}\): C,73.3 H,8.9. Found C, 73.0,72.8; H, 9.5,8.9  
Yield 27 grams or 75\% of the theoretical.  

5-Phenoxy-2-Bromo-Pentane \(\text{C}_8\text{H}_5\text{O}\cdot(\text{CH}_2)_3\text{CHBr}\cdot\text{CH}_3\)  

Thirty-six grams 5-phenoxy-2-hydroxypentane, well cooled with ice, were treated with 30 grams phosphorous tribromide. After the addition of all the phosphorous tribromide the mixture was warmed on the water bath for 30 minutes to complete the reaction and then
poured into ice water. The oily layer was taken up in ether, the ether solution washed with dilute sodium hydroxide, then with water, and finally dried over sodium sulfate. The ether was distilled off on the water bath and the residue fractionated under diminished pressure, collecting the fraction distilling from 165° to 175° at 25 mm. This on redistillation boiled at 171°-173° at 25 mm. The bromide forms a colorless oil boiling at 172° at 26 mm. and with \[ n_D^{30} = 1.529 \text{ and } D_{25}^{30} = 1.258. \]

.2766 gm. subst. gave .2093 gm. AgBr

Calc. for C_{14}H_{18}OBr: Br, 32.9; found Br, 32.2
Yield 36 grams or 75% of the theoretical.

5-Phenoxy-2-Pentene \[ C_9H_5OCH_2CH_2CH=CHCH_3 \]

Thirty grams 5-phenoxy-2-bromopentane and 200 cc. of 10% alcoholic potassium hydroxide were refluxed for ten hours. At the end of this time the mixture was poured into a large excess of water and the oil which separated taken up in ether. The ether solution was dried over sodium sulfate, the ether removed and the residue fractionated under diminished pressure, taking the fraction distilling between 122° and 130° at 25 mm. The product forms a colorless oil with a persistent aromatic odor resembling that of allyl phenyl ether, boiling at 132° under 32 mm. and with \[ n_D^{30} = 1.5005 \text{ and } D_{25}^{25} = .957. \] Under atmospheric pressure the product boils at 226° (uncorrected). Solonina (loc. cit.) gives the boiling point as 236°-227°. Yield 14 grams or 70% of the theoretical.

Attempt To Rearrange 5-Phenoxy-2-Pentene

Twenty grams of the ether was heated to boiling under a re-
flux for twelve hours. The boiling point remained constant at 226° (745 mm.), throughout the entire time, and the material became a very light straw color. All of the ether was recovered unchanged indicating that it not only does not rearrange, but also is stable towards heat.

5-Phenoxy-2-Methyl-2-Pentene

This was prepared by the action of an excess of methyl magnesium iodide upon ethyl \( y \)-phenoxybutyrate:

\[
\text{C}_6\text{H}_5\text{O} \cdot (\text{CH}_2)_3\text{CO} \cdot \text{OEt} + \text{CH}_3\text{MgI} \rightarrow \text{C}_6\text{H}_5\text{O} \cdot (\text{CH}_2)_3\text{O} \cdot (\text{CH}_3)_2 \rightarrow \text{OMgI}
\]

Most of the ethyl \( y \)-phenoxybutyrate used in this research was prepared by esterification of \( y \)-phenoxybutyric acid, which in turn was prepared according to the method of Bentley, Haworth and Perkin as modified by Leuchs.\(^{27}\)

\( y \)-Phenoxybutyric Acid \( \text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2\text{CH}_2 \cdot \text{CH} = \text{CH} \cdot (\text{CH}_3)_2 \)

Three hundred twenty grams (2 mols) of malonic ester were added to a solution of 23 grams (1 atom) of sodium in 500 cc. of absolute alcohol, and the mixture treated with 201 grams (1 mol) of \( y \)-bromophenetole. The whole was then refluxed for three hours. At the end of this time most of the alcohol was distilled off, the residue diluted with water and extracted with ether. The ether solution was dried over \( \text{CaCl}_2 \), the ether removed on the water bath and the residue distilled up to 150° at 20 mm. The distillate consisting of the excess of malonic ester and some unchanged \( y \)-bromophenetole,
was fractionated and these recovered. The residue in the flask was then refluxed for four hours with 1000 cc. of 10% alcoholic potassium hydroxide. Most of the alcohol was then distilled off, the residue diluted with ice and acidified with concentrated hydrochloric acid, when the \( \beta \)-phenoxyethylmalonic acid separated out. This was filtered off, instead of extracted with ether, as recommended by Bentley, Haworth and Perkin (loc. cit.), dried, and, without further purification, converted into the \( \beta \)-phenoxybutyric acid.

The \( \beta \)-phenoxyethyl malonic acid, prepared as described above, was heated in an oil bath to 160° until violent evolution of carbon dioxide ceased. The temperature was then raised to 200° and maintained there for five minutes. On cooling, the \( \beta \)-phenoxybutyric acid solidified to a dark brown crystalline mass, from which the pure acid was obtained by recrystallization from ligroin as white plates melting at 64°.

Ethyl \( \gamma \)-Phenoxybutyrate \( \text{C}_6\text{H}_5\text{O} \cdot (\text{CH}_2)_3\text{COOC}_2\text{H}_5 \)

Ninety grams (.5 mol) of \( \beta \)-phenoxybutyric acid were dissolved in 500 cc. of absolute alcohol, the solution saturated with dry hydrogen chloride, and refluxed for two hours. On cooling, the reaction mixture was diluted with water and extracted with ether. The ethereal solution was washed with dilute sodium carbonate solution, then with water, and finally dried over sodium sulfate. After removal of the ether, the residue was fractionated under diminished pressure, when practically all distilled over between 165° and 180° at 25 mm. This on redistillation boiled at 170° to 173° at 25 mm.
The ester is a colorless rather viscous liquid with a faint unpleasant odor $\eta_D^{33} = 1.491$; $D_{25}^{33} = 1.048$

.2834 gm. subst. gave .7200 gm. CO$_2$ and .1984 gm. H$_2$O

Found C, 69.3; H, 7.8. Calc. for C$_{12}$H$_{16}$O$_3$ c, 69.3; H, 7.7

Later in the course of this work it was found more convenient to prepare the ethyl $\gamma$-phenoxybutyrate from the corresponding nitril.

Ninety grams of $\gamma$-phenoxybutronitril, prepared as described under the preparation of 4-phenoxybutene, were dissolved in 300 cc. of absolute alcohol, 100 cc. concentrated H$_2$SO$_4$ added and the mixture refluxed for five hours. After cooling, the mixture was diluted with ice and extracted with ether. The ether solution was dried over sodium sulphate, the ether removed and the residue distilled, collecting the fraction distilling between 165° and 190° at 25 mm., which on redistillation boiled at 170°-173° at 25 mm., and was identical with that prepared from the acid.

5-Phenoxy-2-Methyl-2-Pentene $\text{C}_6\text{H}_6\text{O} \cdot \text{CH}_2\text{CH}_2\text{CH} = \text{C}$(CH$_3$)$_2$

Twenty-seven grams magnesium were dissolved in 160 grams of methyl iodide in the presence of 400 cc. dry ether. This solution was then added drop by drop to a well cooled solution of 104 grams ethyl phenoxybutyrate dissolved in 300 cc. dry ether. After the addition of all of the Grignard reagent the mixture was allowed to stand over night at room temperature. The solution was then poured into ice, acidified with concentrated hydrochloric acid, the ether layer removed, washed with dilute sodium bisulfite solution to remove some dissolved iodine and dried over sodium sulphate. After
removal of the ether the residue was fractionated. After three fractionations, two main fractions were obtained, the larger one distilling between 137° and 138° at 25 mm., and a smaller one distilling between 166° and 167° at 30 mm.

The lower boiling larger fraction was identified as the 5-phenoxy-2-methyl-2-pentene.

0.2548 gm. subst. gave 0.7564 gm. CO₂ and 0.3114 gm. H₂O

Round C, 81.2; H, 9.2. Calc. for C₁₂H₁₆O c, 81.8; H, 9.1

This substance is a water white, mobile liquid, with a pleasant odor, boiling at 137°-138° at 25 mm., and 241° at 745 mm., with nD = 1.505. It combines readily with bromine and decolorize permanganate solution.

Attempt To Rearrange 5-Phenoxy-2-Methyl-2-Pentene

Twenty grams of the ether were heated to boiling under a reflux for 12 hours. The temperature remained constant at 241° to 242° during this time and the material took on a light straw color. The ether was recovered unchanged, indicating that the ether not only does not rearrange, but also that it is exceptionally stable towards heat.

Examination Of the Fraction Boiling At 166° at 30 mm.

This fraction, a colorless liquid with nD = 1.500, was not identified. The analysis corresponds with the formula C₁₀H₁₄O₂, but due to lack of time it was not further investigated.
I.  .2561 gm. subst. gave .6654 gm CO₂ and .2056 gm. H₂O
II.  .2546 gm. subst. gave .7505 gm CO₂ and .2152 gm. H₂O
III. .1808 gm. subst. gave .4800 gm CO₂ and .1328 gm. H₂O
IV.  .2150 gm. subst. gave .5684 gm CO₂ and .1711 gm. H₂O

Calc. for C₁₀H₁₄O₂ : C, 72.3; H, 8.4

Found: I  C, 72.3; H, 8.4; II  C, 71.9; H, 8.4; III  C, 72.4; H, 8.3; IV  C, 72.1; H, 8.9

Phenoxyethylene

Phenoxyethylene was prepared by the method of Wohl and Berthold from ω-bromophenetole and solid NaOH:

\[
\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2\text{CH}_2\text{Br} \quad \text{NaOH} \quad \text{C}_6\text{H}_5\text{O} \cdot \text{CH}=\text{CH}_2 \quad \text{NaBr} \quad \text{H}_2\text{O}
\]

Phenoxyethylene  \( \text{C}_6\text{H}_5\text{O} \cdot \text{CH}=\text{CH}_2 \)

One hundred grams ω-Bromophenetole and 200 grams powdered NaOH were mixed in a 500 cc. copper flask and distilled from an oil bath at 250°-300°. The distillate was extracted with ether, the ether solution dried over sodium sulphate, the ether removed and the residue distilled. The phenoxyethylene was obtained as a pleasant smelling very mobile liquid boiling at 155°-156°, \( \eta_D^{20} = 1.520 \). Yield 25 grams or 40% of the theoretical.

Attempts to Rearrange Phenoxyethylene

1. Twenty grams of the ether were heated to boiling under a reflux for twelve hours. During this time the boiling point remained constant at 162° (bulb of thermometer in liquid). At the end of this time the contents of the flask, which were a light straw
color, were distilled. All distilled between 155° and 160°. A rearrangement would result in the formation of either

\[
\begin{align*}
\text{o-Vinylphenol} & \quad \text{B. P.} \; 108°/15 \; \text{mm.} \\
\text{Coumaran} & \quad \text{B. P.} \; 188°-190°
\end{align*}
\]

As coumaran boils 30° higher than the phenoxyethylene, and o-vinyl phenol decomposes when distilled at atmospheric pressure (Fries and Fickeworth, loc. cit.), the constancy of the boiling point throughout the heating is sufficient evidence that no rearrangement has taken place.

2. Twenty grams of phenoxyethylene were heated to 260° to 280° in a sealed tube for twelve hours. At the end of this time the contents of the tube, light brown in color, were fractionated. Most distilled between 155° and 165°. This was identified as unchanged ether. The fraction boiling below 155° (1 gm.) possessed a very strong piercing odor. On account of the small quantity it could not be identified. The fraction boiling between 165° and 190° (4 gms.) was dissolved in ether and the ethereal solution extracted with cold dilute potassium hydroxide. The alkaline solution on acidification deposited a small quantity of a reddish oil which was identified as phenol.

\[
p\text{-Tolyloxyethylene} \quad \text{CH}_3\text{OCH} = \text{CH}_2.
\]
This was prepared in the same manner as the phenoxyethylene, starting with p-cresol. \(^{31}\) p-Tolyloxyethyl bromide is a colorless crystalline solid, melting at 40°, and boiling at 254°-255°.

Distilled with solid NaOH, this bromide yielded p-tolyloxyethylene as a colorless, mobile liquid, with an odor very much like that of the phenoxyethylene, boiling at 177°-180°. \(^{30}\) \(N_D = 1.513, \quad D_{25} = .975.\)

.2504 gm. subst. gave .737 gm. CO\(_2\) and .1630 gm. H\(_2\)O

Found C, 80.3; H, 7.2

Calc. for C\(_9\)H\(_{10}\)O: C, 80.6; H, 7.5

Attempts To Rearrange p-Tolyloxyethylene

1. Twenty grams of p-tolyloxyethylene were heated in a sealed tube to 230° for ten hours. Upon cooling, the contents of the tube, a very viscous dark red-brown tar, were dissolved in ether, and the ethereal solution extracted with 10% potassium hydroxide solution.

Upon acidifying the alkaline solution, a light red oil separated out. This was taken up in ether, the ether solution dried over sodium sulfate and the ether removed. Ten grams of a brown oil remained. This possessed a strong phenolic odor, gave a deep blue color with ferric chloride and formed a p-nitrobenzoate, melting at 99°. A sample of p-tolyl p-nitrobenzoate prepared from pure p-cresol melted at 99° and a mixture of the two also melted at 99°. Furthermore, this oil distilled almost completely between 124° and 125° at 60 mm. A sample of pure p-cresol also boiled at 124° at 60 mm. The alkali soluble decomposition product was thus
identified as p-cresol.

The ether solution containing the alkali insoluble decomposition products was washed with water and dried over sodium sulfate. After removal of the ether, a dark red tar remained. No definite compound could be obtained from this.

2. Ten grams of p-tolyloxyethylene were heated to boiling under a reflux for two hours. The temperature rose rapidly from 175° to 315° where it remained constant. The contents of the flask, a dark red-violet viscous liquid, were dissolved in ether and the ethereal solution extracted with 10% potassium hydroxide solution.

Upon acidifying the alkaline solution a colorless oil separated out. This gave a deep blue color with ferric chloride and formed a p-nitrobenzoate melting at 99°. The alkali soluble decomposition product was thus identified as p-cresol, as in the previous trial.

The ether solution, containing the alkali insoluble decomposition products, was washed with water and dried over sodium sulfate. After removal of the ether, 5 grams of a transparent sticky brown residue remained. This was fractionated and yielded two fractions: (1) below 180° at 45 mm., and (2) 180° to 300° at 45 mm. Fraction 1 came over between 200° and 220° at 745 mm., as a colorless liquid which became violet-red over night. Fraction 2 was a viscous red brown liquid. Due to the small quantity of material these two fractions could not be identified, and due to the impossibility of obtaining more p-cresol, the work could not be repeated.
Phenylpropargyl Ether

The phenylpropargyl ether was prepared according to the method of Henry by action of alcoholic potash upon phenyl $\beta$-bromoallyl ether:

$$C_6H_5O\cdot CH_2\cdot CBr=CH_2 + KOH \rightarrow C_6H_5O\cdot CH_2\cdot C=CH + KBr + H_2O$$

The phenyl $\beta$-bromoallyl ether was prepared in part by the action of sodium phenolate upon bromallylbromide,

$$C_6H_5O\cdot Na + BrCH_2\cdot CBr=CH_2 \rightarrow C_6H_5O\cdot CH_2\cdot C=CH + NaBr$$

However, the majority of the phenyl $\beta$-bromoallyl ether used in this work was obtained by the action of an excess of alcoholic sodium phenolate upon tribromhydrin,

$$2C_6H_5ONa + CH_2Br\cdot CHBr\cdot CH_2Br \rightarrow C_6H_5O\cdot CH_2\cdot CBr=CH_2 + C_6H_5OH + 2NaBr$$

Tribromhydrin \hspace{1cm} \textit{$CH_2Br\cdot CHBr\cdot CH_2Br$}

Two hundred forty grams of allyl bromide were dissolved in 500 cc. of dry carbon disulphide, and a solution of 320 grams of bromine in 200 cc. of carbon disulphide added drop by drop, keeping the temperature below 10°. The carbon disulphide was then distilled off and the residue distilled, collecting the fraction boiling between 218° and 225°. Yield 500 grams of practically pure tribromhydrin, corresponding to 90% of the theoretical.

Bromallylbromide $^{33}$ \hspace{1cm} \textit{$CH_2Br\cdot CBr=CH_2$}

Two hundred eighty grams of tribromhydrin were dissolved in 500 cc. of dry ether and 35 grams of sodium added and the mixture allowed to stand over night. The ether solution was then filtered
from the sodium bromide and unchanged sodium, and the ether distilled off. The residue on distillation came over between 145° and 155°. Yield 105 grams or 52% of the theoretical.

Phenyl β-Bromallylether \[ \text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CBr} = \text{CH}_2 \]

Fifty grams of phenol were added to a solution of 12 grams of sodium in 200 cc. of absolute alcohol. 100 grams of bromallylbromide were then added. A violent reaction took place, with copious separation of sodium bromide. The mixture was allowed to stand for thirty minutes, then diluted with water and extracted with ether. The ether solution was washed twice with dilute sodium hydroxide solution, once with water and dried over sodium sulfate. After removal of the ether, the residue was distilled, collecting the fraction boiling from 235° to 245°. As the ether does not boil without decomposition at atmospheric pressure, it was redistilled under diminished pressure. B. P. 135° at 30 mm. \( D_{20}^0 = 1.395 \), \( N_D^0 = 1.554 \). Yield 74 grams or 70% of the theoretical.

Action Of Sodium Phenolate On Tribromhydrin

Preparation Of β-Bromallylphenyl Ether

As the foregoing preparation of β-bromallyl phenyl ether is rather tedious and does not give very good yields, another method was sought. When tribromhydrin is treated with sodium ethylate, β-bromallylethyl ether is formed, and it was thought that sodium phenolate would have an analogous effect.

Twenty-four grams of sodium were dissolved in 300 cc. absolute alcohol and 94 grams of phenol added to the hot solution. 135 gms.
of tribrom hydrin were then added. A very violent reaction took place, with immediate, copious, precipitation of sodium bromide. The alcohol was then distilled off as well as possible, the residue diluted with water, extracted with ether, the ether extract washed twice with dilute sodium hydroxide solution and once with water, and then dried over sodium sulphate. After removal of the ether, the residue was distilled under diminished pressure, taking the fraction distilling between 125° and 135° at 25 mm. On redistillation this boiled at 135° at 30 mm. \( D_{20} = 1.396, n_D^2 = 1.554. \) The product was thus identified as phenyl \( \beta \)-bromallyl ether. Yield 84 grams or 83% of the theoretical.

Phenylpropargyl Ether \( \text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{C} = \text{CH} \)

One hundred seven grams of phenyl \( \beta \)-bromallyl ether were boiled under a reflux with 350 cc. of 2N alcoholic potassium hydroxide for four hours. The alcohol was then removed as completely as possible on the water bath. The residue was diluted with water, extracted with ether and the ether solution dried over sodium sulfate. After removal of the ether, the residue was distilled under diminished pressure, taking the fraction distilling between 108° and 120° at 40 mm. This on redistillation boiled constant at 111° to 113° at 40 mm. At atmospheric pressure it boils with slight decomposition at 209°. Henry gives 210° as the boiling point. \( N_D^2 = 1.535, D_{16}^2 = 1.04. \) Yield 35 grams or 53% of the theoretical.

Attempts to Rearrange Phenylpropargyl Ether

1. Twenty grams of phenylpropargyl ether were heated to boil-
ing under a reflux for five hours. On cooling the contents of
the flask solidified to a solid black tar, from which no definite
substance could be isolated. The ether had apparently decomposed
completely.

2. Twenty grams of phenylpropargyl ether were dissolved in
100 grams of di-isoamyl ether (B. P. 170°) and the whole heated to
boiling for one hundred hours. After several hours heating a
dark brown solid began to separate out and the solution darkened
somewhat. The solution was then filtered from this dark brown
humus like substance, and extracted twice with 10% potassium
hydroxide solution. Acidification of the combined alkaline
extracts produced a slight cloudiness, and more of the humus-like
substance separated out.

3. Twenty grams of phenylpropargyl ether were heated in a
bath of boiling di-isoamyl ether (B. P. 170°) for twenty hours.
The substance became first straw colored and finally black. It
was then cooled, dissolved in ether, and the ether solution extract-
ed twice with 10% potassium hydroxide. The combined alkaline
solutions gave a faint cloudiness when acidified with dilute sul-
phuric acid. The ether solution was dried over sodium sulphate,
the ether removed, and the residue distilled. 17 grams of an oil
distilling between 125° and 135° was obtained, besides a small
amount of tar which remained in the distilling bulb. This frac-
tion was identified as unchanged phenylpropargyl ether.

4. Twenty grams of phenylpropargyl ether and 20 grams of di-
ethylaniline were heated to boiling under a reflux for five hours,
during which time the boiling point remained constant at 205°.
The mixture was then filtered from a small quantity of carbonaceous
matter, taken up in ether, and the ether solution washed twice with
dilute acid to remove the diethylaniline. The solution was then
extracted with dilute alkali. The alkaline solution gave no pre-
cipitate upon acidification. From the ether solution 10 grams of
unchanged phenylpropargyl ether was recovered.

p-Bromphenyl \( \beta \)-bromallylEther \( \text{BrC}_6\text{H}_4\text{O} \cdot \text{CH}_2 \cdot \text{CBr}=\text{CH}_2 \)

This ether, prepared, in the same manner as the corresponding
phenyl ether, from tribromhydrin and 2 mols. of alcoholic sodium
phenolate, boils at 171° at 22 mm. \( N^2_{22} = 1.567, D_{25} = 1.719. \)

I. \( 0.3852 \text{ gm.} \) gave \( 0.4928 \text{ gm. AgBr} \)
II. \( 0.2402 \text{ gm.} \) gave \( 0.3054 \text{ gm. AgBr} \)
III. \( 0.3194 \text{ gm.} \) required \( 31.61 \text{ cc. N/10 AgNO}_3 \)
IV. \( 0.2998 \text{ gm.} \) required \( 20.44 \text{ cc. N/10 AgNO}_3 \)
Calculated for \( \text{C}_9\text{H}_8\text{OBr}_2 \): \( \text{Br}, 54.7 \)
Found: \( \text{Br}, 54.1, 54.4, 54.1, 54.5 \)
Yield 70% of the theoretical

p-Bromophenyl Propargyl Ether \( \text{BrC}_6\text{H}_4\text{O} \cdot \text{CH}_2 \cdot \text{C=}\text{CH} \)

This ether was prepared from the above ether by treatment
with 2N alcoholic KOH, as in the case of the phenyl ether, boiling
at 144° at 24 mm.

\( ^{(1)} \) Analyses III and IV were carried out by Mr. W. A. Van
Winkle in connection with his work upon "The Determination Of The
Halogens In Volatile Organic Compounds".
\[ N_D^3 = 1.567, \quad D_{25}^3 = 1.468 \]

.3688 gm. subst. gave .3377 gm. AgBr

.3942 gm. subst. gave .3609 gm. AgBr

Calc. for C_9H_7OBr: Br, 38.0

Found: Br, 39.0, 39.0

Yield 50\% of the theoretical.

Attempt To Rearrange p-Bromphenylpropargyl Ether

1. Twenty grams of p-bromphenylpropargyl ether were heated to boiling under a reflux for thirty minutes. The temperature rose rapidly from 254\(^\circ\) to 268\(^\circ\). Finally the contents of the flask became almost solid. Upon cooling the mass set to a brittle tar, indicating almost complete carbonization.

2. Twenty grams of p-bromphenylpropargyl ether were dissolved in 100 grams of di-isoamyl ether and the solution heated to boiling for ten hours. The cooled solution was then extracted with dilute potassium hydroxide. The alkaline solution gave no precipitate upon acidification.

Phenoxyacetonitril

\[
\text{O-CH}_2\text{-CN}
\]

This substance was prepared according to the method of Fritsche, with slight modification. Phenol and chloracetic acid react under the influence of aqueous sodium hydroxide give the sodium salt of phenoxyacetic acid:

\[
\text{CH}_2\text{Cl} \cdot \text{COOH} + \text{C}_6\text{H}_5\text{OH} + 2\text{NaOH} \rightarrow \text{C}_6\text{H}_5\cdot \text{O} \cdot \text{CH}_2 \cdot \text{COONa} + \text{NaCl} + 2\text{H}_2\text{O}
\]

The free acid on treatment with alcohol and dry hydrogen chloride
yields the ethyl ester, which is converted by treatment with aqueous ammonia into the amid. The amid yields the nitril on distillation with phosphorus pentoxide:

\[ \text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH} \rightarrow \text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5 \]

\[ \text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CONH}_2 \rightarrow \text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}=\text{N} \]

Preparation Of Phenoxyacetic Acid \text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}^{38}

One hundred eighty-eight grams of phenol and 180 grams monochloracetic acid were melted up together in a large porcelain dish. Then a solution of 200 grams of sodium hydroxide in 500 cc. water was cautiously added, stirring vigorously. The mixture became very hot, volatilizing a large quantity of water. On cooling, the entire contents of the dish set to a solid mass. This was freed from excess sodium hydroxide by suction and dissolved in 500 cc. boiling water. This solution was then made strongly acid with hydrochloric acid, when the phenoxyacetic acid separated as an oil. On cooling, however, this oil solidified to a mass of crystals, which were filtered off and dried. Yield 250 grams or 80% of the theoretical.

Ethyl Phenoxyacetate \text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5^{39}

One hundred fifty-two grams of phenoxyacetic acid were dissolved in 150 grams of absolute alcohol and heated on the water bath for 1-1/2 hours, while a continuous stream of dry hydrogen chloride was passed into the solution. At the end of this time the contents of the flask were poured into an excess of water, the oily layer removed, the aqueous layer extracted once with ether and the oily
layer and the ether extract united. The ether was then distilled off on the water bath, and the residue distilled, collecting the fraction boiling from 245° to 265°. On redistillation the ester boiled at 251° at 745 mm. Yield 158 grams or 68% of the theoretical.

Phenoxyacetamid $\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$

One hundred eighty grams of phenoxyacetic ester was covered with twice its volume of concentrated ammonia solution and allowed to stand until the entire oily layer had set to a solid mass (2 to 4 days). The aqueous solution was removed by filtration and the amid recrystallized from hot water, from which it crystallized in fine needles, melting at 101°. Yield 125 grams or 83% of the theoretical.

Phenoxyacetonitril $\text{C}_6\text{H}_5\text{O} \cdot \text{CH}_2 \cdot \text{CN}$

Fritzsche (loc. cit.) recommends distilling an intimate mixture of the amid and phosphorus pentoxide. This procedure is accompanied by very much charring and frothing, and the yields are poor, never over 30%. The procedure was therefore modified in the following fashion: 75 grams of dry phenoxyacetamid were placed in a 500 cc. distilling flask and melted completely. The 60 grams of phosphorus pentoxide were poured directly into the molten amid and the whole distilled as rapidly as possible. The distillate, containing both the nitril and unchanged amid, was treated with dry ether, in which the amid is practically insoluble, and filtered. The ether was removed from the filtrate and the residue, distilled in vacuum. The nitril is a colorless oil boiling at 132° at 30
mm. and 235° at 745 mm.

Attempt to Rearrange Phenoxyacetonitrile.

1. Twenty-five grams of phenoxyacetonitrile were heated to boiling under a reflux for fifteen hours. The liquid became first yellow then red, and finally black, but the temperature remained constant at 242°. At the end of this time the contents of the flask were distilled and 22 grams of nitril distilling between 232° and 238°. Two repetitions of the attempt led to the same result.

p-Tolyloxyacetonitril \( \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{O} \cdot \text{CH}_2\text{CN} \)

p-tolyloxyacetic acetic acid, prepared from p-cresol and chloracetic acid in the same manner as the phenoxyacetic acid, crystallizes from hot water in needles melting at 135°. Yield 74% of the theoretical.

Ethyl p-tolyloxyacetate, obtained by esterification of the acid, forms a colorless pleasant smelling liquid boiling at 266° to 267° at 740 mm. Hewitt, Johnson and Pope obtained the ester from sodium p-cresolate and ethyl chloroacetate, and give 243° at 752 mm. as the boiling point. A sample of the ester was then prepared according to the directions given by these writers and it also boiled at 266° to 267°, at 740 mm. The temperatures are uncorrected.

p-tolyloxyacetamid was prepared from the ester by treatment with aqueous ammonia at room temperature as in the preparation of phenoxyacetamid. The amid crystallizes from hot water in fine needles, melting at 127°. Forte, who obtained the amid by distilling a
mixture of methyl p-tolyloxyacetate and aqueous ammonia, gives 126°-127° as the melting point.

The amid was distilled with phosphorus pentoxide, observing the same precautions as in the case of the phenoxy- compound. The nitril was obtained as a colorless, pleasant smelling oil boiling at 148°-149° at 28 mm. On cooling it solidified to a mass of crystals melting at 40°. Stoermer, who prepared the nitril by dehydration of p-tolyloxyacetaldoxime with acetic anhydride, gives 40° as the melting point.

Attempt to Rearrange p-Tolyloxyacetonitril

1. Twenty-five grams of p-tolyloxyacetonitril were heated to boiling under a reflux for twenty-four hours. On cooling the entire contents of the flask set to a solid brittle tar, indicating almost complete carbonization.

2. Twenty-five grams of p-tolyloxyacetonitril were heated in a bath of boiling di-isoamyl ether (B. P. 170°) for fifteen hours. The substance was then fractionated under diminished pressure, collecting two fractions. The high boiling fraction on redistillation proved to be unchanged p-tolyloxyacetonitril. The low boiling fraction (5 grams) was dissolved in ether and extracted with dilute potassium hydroxide solution. The alkaline solution deposited a small quantity of an oil, upon acidification. This was identified as p-cresol.

3. Twenty-five grams of p-tolyloxyacetonitril were dissolved in 100 grams of di-isoamyl ether and the solution boiled for ninety
hours at 170°. At the end of this time it was filtered from some carbon which had separated out, and, extracted twice with dilute alkali. The alkaline solution on acidification, deposited a small quantity of p-cresol. From the ether solution the majority of the original nitril was recovered unchanged.
Benzyl Ethers

\[
\text{Etc.}
\]

The ethers were prepared by refluxing a mixture of equimolecular quantities of the phenol, benzyl chloride and potassium carbonate, with acetone as a diluent.

Phenylbenzyl Ether \( \text{C}_6\text{H}_5\cdot\text{O} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5 \)

One hundred twenty-six grams of benzyl chloride (1 mol), 105 grams of phenol (1.1 mol), 138 grams of potassium carbonate and 100 cc. of acetone were refluxed on the water bath for eight hours. After dilution with water, the benzylphenyl ether was taken up in ether, the ether solution washed with dilute alkali, then with water, and finally dried over sodium sulfate. After removal of the ether, the residue was fractionated under diminished pressure. By two fractionations the benzyl phenyl ether was obtained as a colorless liquid distilling at 178° to 179° at 35 mm., and at 171° to 173° at 22 mm. It solidified on cooling to a mass of colorless crystals melting sharply at 39°.

Attempts to Rearrange Phenyl Benzyl Ether

1. 100 grams of phenyl benzyl ether were heated boiling under a reflux for four hours. The temperature of the liquid rapidly dropped from 272° to 220°. The contents of the flask, a viscous, dark red liquid were taken up in ether and the ether solution extracted with dilute potassium hydroxide solution. Upon acidifying the alkaline solution, a reddish oil separated out. This was identified as phenol. The ether solution was dried and the ether
removed. The residue was then distilled, yielding three fractions. The lowest fraction was found to contain toluene, boiling at 110° and readily oxidized to benzoic acid, melting at 120°. The second fraction, on repeated fractionation yielded a colorless liquid boiling at 172° to 173° at 22 mm., which was identified as unchanged benzyl phenyl ether, and another colorless liquid boiling at 185° to 190° at 22 mm. This would not solidify in an ice-salt mixture, nor was it soluble in alkali. As it was not phenolic in character, it was not further investigated. The high boiling fraction was a very thick brown oil, insoluble in alkali. It was not further investigated.

2. The attempt was repeated, with the same results.

p'-Bromphenyl Benzyl Ether  \( \text{BrC}_6\text{H}_4\text{O} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5 \)

This was prepared in the same manner as the foregoing with slight modification. The reaction mixture, after dilution with water, was not extracted with ether, but was treated with cracked ice, whereupon the p-bromphenyl benzyl ether solidified to a pasty mass. This was filtered off and crystallized from alcohol, from which it separates in long thick needles melting at 64° and boiling at 226° at 50 mm.

Attempts to Rearrange p'-Bromphenyl Benzyl Ether

1. One hundred grams of p-bromphenyl benzyl ether were heated to boiling under a reflux. The ether began to boil regularly at 310°, but decomposition immediately set in and the temperature rapidly dropped to 250°. It was then dissolved in ether and the
ether solution extracted with dilute alkali. The addition of
the alkali produced a beautiful violet color, which however dis-
appeared upon the addition of a large excess.

The alkaline solution was acidified with dilute sulphuric acid
and the oil which separated out taken up in ether. After re-
moving the ether, the residue was fractionated under diminished
pressure. With the exception of a very little low and high boil-
ing material, everything distilled between 140° and 150° at 35 mm.
This was identified as p-bromphenol.

The ether solution, containing the alkali insoluble decomposi-
tion products, was dried over sodium sulphate and the ether removed.
The residue was then distilled at atmospheric pressure. A small
quantity of a very mobile liquid distilled over until the tempera-
ture reached 190°. Then, suddenly, violent decomposition set in,
with the evolution of clouds of hydrogen bromide. The contents of
the flask set to brittle mass of tar on cooling. The small quan-
tity liquid was fractionated and found to distill between 175° and
185°. It violently attacked the eyes and nose. It was probably
benzyl bromide.

2. The attempt was repeated, continuing the heating for a long-
er time. The ether began to boil at 310°, but the temperature
rapidly dropped to 230°, with continual evolution of hydrogen brom-
ide. The contents of the flask, a dark red brown, very viscous
liquid was fractionated under diminished pressure, collecting three
fractions. The first fraction consisted of a small quantity of the
compound boiling at 175° to 185° at 745 mm. The middle fraction was taken up in ether and the ether solution extracted with dilute alkali. Upon acidifying the alkaline solution, a considerable quantity of p-bromophenol was obtained. The ether solution was dried and the ether removed. The residue was united with fraction No. 3 and they were refractionationed, obtaining a liquid distilling between 225° and 230° at 60 mm. This soon solidified to a mass of crystals melting at 63°. Recrystallized from alcohol they melted at 65°, thus indicating that the substance was unchanged p-bromophenyl benzyl ether.

Nitrobenzyl Ethers

\[ \text{O - CH}_2 - \text{NO}_2 \]

The p-nitrobenzyl ethers were prepared in the same manner as the benzyl ethers, from p-nitrobenzyl chloride and the appropriate phenol.

Preparation of p-Nitrobenzylchloride

This was prepared according to the method of Allway, \(^\text{46}\) by nitratation of benzyl chloride in the cold. To 360 grams benzyl chloride cooled with an ice-salt mixture, were added drop by drop with constant stirring, a mixture of 270 grams nitric acid (D = 1.52), and 300 cc. concentrated sulphuric acid. As soon as all of the acid had been added, the mixture was poured into cracked ice and allowed to stand some time. The water was then decanted, the pasty mixture of p-nitrobenzyl chloride and o-nitrobenzyl chloride
filtered with suction and the p-nitrobenzyl chloride crystallized from alcohol. It crystallized from alcohol in long yellow needles melting at 71°. Yield 135 grams or 25% of the theoretical. Allway claims 50% yields, but in eight runs by the foregoing method the yields never exceeded 28% nor fell below 22%.

Since this work was done, a convenient method for the preparation of p-nitrobenzyl bromide has appeared. The method consists in brominating p-nitrotoluene in carbon tetrachloride solution in the sunlight, using iodine as a catalyst.

Phenyl p-Nitrobenzyl Ether \( \text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \)

This was prepared in the same manner as the benzyl ether from phenol, p-nitrobenzyl chloride and potassium carbonate in the presence of acetone. The ether crystallizes from alcohol in fine yellow needles melting at 91°.

In the same manner were prepared:

o-Tolyl p-Nitrobenzyl Ether \( \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \)

The ether crystallizes from alcohol in long thick yellow needles melting at 90°. The melting point agrees with that given by Reid (loc. cit.).

p-Tolyl p-Nitrobenzyl Ether \( \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \)

This crystallizes from alcohol in thick yellow leaves melting at 89°. Reid gives 88°. The three following ethers, prepared in the same manner, are not recorded in the literature.

p-Methoxyphenyl p-Nitrobenzyl Ether \( \text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \)

This ether crystallizes from alcohol in dark yellow needles
melting at 88°

p-Bromphenyl p-Nitrobenzyl Ether $\text{BrC}_6\text{H}_4\cdot\text{O} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$

This ether crystallizes from alcohol in fine needles melting at 112°.

2,4-Dibromphenyl p-Nitrobenzyl Ether $\text{Br}_2\text{C}_6\text{H}_3\text{O} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$

This ether crystallizes from alcohol in short fine needles melting at 161°.

The nitrobenzyl ethers charred completely when heated to their boiling points. At lower temperatures the decomposition was slower, but nevertheless complete, if the heating was continued long enough. When the heating at the lower temperatures, 200° to 220°, was not long continued, part of the original ether could be recovered unchanged, but no other products could be isolated.

Brombenzyl Ethers

\[ \text{Br} - \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \]

p-Brombenzyl Bromide

The methods given in the literature for the preparation of this compound are not very satisfactory, as they involve the separation of the p-brombenzylbromide from the o-brombenzylbromide formed at the same time. This is due to the fact that the starting point in the preparation is the mixture of o- and p-bromtoluenes formed by bromination of toluene in the cold. This difficulty was readily avoided by using pure p-bromotoluene obtained from p-toluidine.

One hundred seventy-five grams (1.1 mol) of bromine were
aspirated through 171 grams (1 mol) of pure p-bromotoluene heated to 160° to 190° in an oil bath.

The suction was applied through a long wide air condenser, and between it and the pump were placed two wash bottles containing water and strong sodium hydroxide solution. This precaution was very necessary as the p-bromobenzyl bromide is very volatile and violently attacks the eyes and nose. In fact, it is so bad that one investigator recommends that all work with the reagent be carried on in the open. As soon as all of the bromine was used up, the flask was removed from the oil bath and allowed to cool. The p-bromobenzyl bromide was then crystallized from alcohol, from which it separates in light brown needles melting at 60° (Jackson gives 61°).

p-Bromophenyl p-Bromobenzyl Ether \( \text{BrC}_6\text{H}_4\text{O} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Br} \)

This ether, prepared in the same manner as the other benzyl ethers, crystallizes from alcohol in fine needles, melting at 111°.

Attempt to Rearrange p-Bromophenyl-p-Bromobenzyl Ether

Twenty grams of the ether were heated to 290°. At that temperature violent boiling set in and the temperature rose suddenly to 300° and then dropped rapidly to 265°, when the boiling ceased. The substance was then heated for one minute, when violent decomposition began, with copious evolution of hydrogen bromide. The contents of the flask were then distilled collecting a fraction boiling from 110° to 140° at 90 mm. At 140° the entire mass decomposed with further evolution of hydrogen bromide. The liquid
which distilled between 110° and 140° boiled at 175° to 185° at 745 mm., and was probably p-bromotoluene.

3,4-Dibromphenyl p-Brombenzyl Ether \( \text{Br}_2\text{C}_6\text{H}_3\text{O} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Br} \)

Prepared by the general method, this ether crystallizes from alcohol in long fine needles melting at 100°.

Attempts to Prepare Phenyl 2,4-Dinitrobenzyl Ether

![Diagram of Phenyl 2,4-Dinitrobenzyl Ether]

Apparently no 2,4-dinitrobenzyl ethers are known, none being recorded in the literature. The logical method of preparation seemed to be by the action of sodium phenolate upon 2,4-dinitrobenzyl chloride, either in alcohol solution or in some inert solvent. However, all attempts to prepare the ether failed.

2,4-Dinitrobenzyl Chloride

This was prepared by the method of Friedlander and Cohn.

100 grams finely crystallized p-nitrobenzyl chloride were stirred into 800 grams concentrated sulphuric acid, and then a mixture of 200 grams concentrated sulphuric acid and 65 grams nitric acid (\( D = 1.45 \)) was added drop by drop, stirring continuously and keeping the temperature below 15°. As soon as the acid had been added the clear solution was poured into ice, when the 2,4-dinitrobenzyl chloride separated out as a faint yellow solid. This was filtered with suction and recrystallized from ether, from which it separates as light yellow plates, melting at 34°. The yield is practically quantitative. The compound is only slightly volatile and there-
fore has no effect upon the eyes, but even a trace of the solid raises very painful blisters on the skin.

The preparation of phenyl 2,4-dinitrobenzyl ether was attempted in the following ways:

1. A solution of (.15 mol) sodium phenolate in 100 cc. absolute alcohol was treated with .1 mol. of dinitrobenzyl chloride. Sodium chloride began to separate out immediately, together with a fine yellow powder. The mixture was refluxed for one hour to complete the reaction, most of the alcohol distilled off and the residue diluted with water. The sodium chloride completely dissolved leaving the fine yellow powder mentioned above. This was found to be insoluble in alcohol, ether, acetone, ligroin and boiling amyl alcohol. It was, however, found to be slightly soluble in glacial acetic acid but could not be crystallized from it. It was crystallized from hot nitrobenzene from which it separates in fine yellow needles, melting with violent decomposition at 265°. The substance was evidently 2,4,2,4 tetranitrostilbene, formed in accordance with the reaction:

$$2 \text{O}_2 \text{N-CH}_2 \text{Cl} + 2 \text{ONa} \rightarrow \text{O}_2 \text{N-CH=CH-NO}_2 + 2 \text{C}_6\text{H}_5\text{OH} + 2 \text{NaCl}$$

This tetranitrostilbene has been prepared by the action of alcoholic potash on dinitrobenzyl chloride. Krasuski gives 264°-266° as the melting point and Friedlander and Cohn give 265°.

The reaction was carried out adding the sodium phenolate solution to the dinitrobenzyl chloride with the same result.
2. 0.15 mol. of dry powdered sodium phenolate was added in small portions to a cold solution of 0.1 mol. of 2,4-dinitrobenzyl chloride in 200 cc. dry benzene. The mixture was allowed to stand with frequent shaking, for some time, and then warmed for one hour on the water bath. The mixture was then treated with water, whereupon the sodium chloride and excess sodium phenolate went into solution, leaving a yellow solid, which was identified as tetranitrostilbene.

3. 0.15 mol. of dry powdered sodium phenolate was mixed with 0.1 mol of melted 2,4-dinitrobenzyl chloride. The mass immediately became warm and in less than a minute burst into flame.

4. An attempt to prepare the ether by the general method given above for the preparation of the benzyl ethers also resulted in the formation of tetranitrostilbene.
Phenyl Cinnamyl Ether \( C_6H_5O \cdot CH_2 \cdot CH=CH \cdot C_6H_5 \)

This was prepared by treating cinnamyl bromide with an alcoholic solution of sodium phenolate. It crystallizes from 80% alcohol in fine white needles melting at 70°.

**Calc. for C\(_{16}\)H\(_{14}\)O:** C, 85.7; H, 6.7  
**Found:** C, 85.2; H, 6.7

On account of the high price and scarcity of cinnamyl alcohol, it was impossible to obtain enough phenyl cinnamyl ether to work with. However, as it is not described in the literature, it is included here.
SUMMARY

1. Several new unsaturated phenyl ethers have been prepared and characterized.

2. The methods of preparation of several previously known unsaturated phenyl ethers have been simplified and improved.

3. It has been established that the following types of phenyl ethers do not undergo the Claisen rearrangement:

   \[ C_6H_5O\cdot\text{CH}_2\text{CH}_2\text{CH} = \text{CR}_2 \]
   \[ C_6H_5O\cdot\text{CH} = \text{CH}_2 \]
   \[ C_6H_5O\cdot\text{CH}_2-\text{C} = \text{CH} \]
   \[ C_6H_5O\cdot\text{CH}_2-\text{C} = \text{N} \]
   \[ C_6H_5O\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5 \]
BIOGRAPHY

The writer was born in Seattle, Washington, on December, 31st, 1895. He attended grade and high school there. The school year 1912-1913 he spent at Dartmouth College, Hanover, New Hampshire. During the three years from 1913 to 1916 he attended the University of Washington, where he finished the work required for the degree of Bachelor of Science, in February, 1916. He was granted the degree of Master of Science at the end of the Summer Session in the same year. The three years from 1916 to 1919 he spend as graduate assistant (one year) and assistant in chemistry at the University of Illinois.
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