CXCVI.—*The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides.*

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OBSERVATIONS on the action of epichlorohydrin and of aryl ethers of glycide on alkaline solutions of phenols (Lindeman, *Ber.*, 1891, **24**, 2147; Boyd and Marle, T., 1910, **97**, 1788) have shown that the olefine oxide group reacts readily with sodium phenoxides to produce phenolic ethers:

$$CHR \cdot CH_2 + C_6H_5 \cdot ONa = CHR(ONa) \cdot CH_2 \cdot O \cdot C_6H_5 ;$$
$$\diagdown O \diagup$$
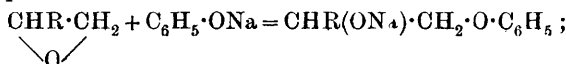
and the reaction appeared to us to be one that might with advantage be studied quantitatively with the object of ascertaining how the speed of combination varies with (i) the constitution of the phenol, and (ii) that of the olefine oxide.

The olefine oxides which we have chosen for investigation are ethylene and propylene oxides.

It was observed by Roithner (*Monatsh.*, 1894, **15**, 674) that the former combines with phenol when heated with it for some hours at 150°. The reaction, however, proceeds much more rapidly in the presence of an alkali, and can, we find, be conveniently carried out in alcoholic solution at temperatures between 50° and 100°.

Method of Experiment.

The following is a brief account of the method which we adopted for carrying out our experiments. Further details will be found in the experimental portion of the paper.

A standard solution of each phenol in 98 per cent. ethyl alcohol was prepared, and a suitable quantity of this was mixed with sodium ethoxide solution and ethyl alcohol in the proportions necessary to produce a liquid normal as regards the amount of phenol and twentieth normal as regards the sodium present. The ethylene or propylene oxide was weighed in a sealed bulb, the amount taken varying in most cases between 0·1 and 0·5 gram. The bulb was placed in a glass tube along with an equivalent quantity of the alkaline phenol solution, and the tube was then sealed at the blowpipe, care being taken to prevent the introduction of any carbon dioxide during the process. In the majority of the experiments the reaction tube was of such a length that the space unoccupied by the reaction liquid was about one and a-half times or twice the volume of the liquid; but it was found that an increase of the air space up to at least three times the volume

of the liquid present had no important influence on the speed of
the reaction. After the bulb containing the olefine oxide had
been broken, the reaction tube was placed in a thermostat at $70\cdot4^\circ$
and heated for one hour or longer. It was then quickly cooled
and opened, and the contents were transferred to a separating
funnel. Ether was added (or in some cases light petroleum), and
the ethereal solution was shaken repeatedly with a dilute solution
of potassium hydroxide, until the alkaline washings were found
to be free from phenol. The series of alkaline liquors was then
shaken two or three times with fresh quantities of ether. The
combined ethereal solutions were dried over potassium carbonate,
and the ether distilled off from a tared flask. The resultant glycol
aryl ether was dried for some hours in a vacuum desiccator over
sulphuric acid, and then weighed.

Preliminary experiments in which the olefine oxides were heated
with $N/20$-sodium ethoxide solution in the absence of any phenol,
and the process otherwise carried out as above indicated, resulted
in no weighable quantity of product being obtained on evapora-
tion of the ether.

Theory of the Reaction.

Ethylene oxide, as already stated, can combine with phenols in
the absence of alkali, but at $70\cdot4^\circ$ the temperature employed in
our experiments, the speed of combination in the case of the less
acidic phenols is small in comparison with the speed with which
the oxide unites with the sodium phenoxide. This is shown by the
following figures obtained in the case of p-cresol:

Reaction solution.	Percentage of ethylene oxide converted into glycol p-tolyl ether in 2 hours at $70\cdot4^\circ$.
(i) N-p-Cresol	$1\cdot0$
(ii) N-p-Cresol, $N/20$-Na$^\cdot$	$72\cdot5$

The yield of glycol p-tolyl ether obtained in the second case is
thus due almost entirely to the sodium p-tolyloxide; and since the
concentration of the sodium tolyloxide must remain constant so
long as a considerable excess of p-cresol is present, it follows that
the rate of formation of glycol p-tolyl ether during the greater
part of the reaction-time must be approximately in accordance
with the formula for a unimolecular reaction. The following
figures illustrate this:

| Reaction solution.	Time of heating.	Yield of glycol p-tolyl ether. Per cent.	$k = \dfrac{1}{t} \log \dfrac{100}{100-x}$
N-p-Cresol $N/20$-Nai	1 hour	$47\cdot0$	$0\cdot276$
	2 hours	$71\cdot8$	$0\cdot275$
	2 ,,	$73\cdot2$	$0\cdot286$

In the case of propylene oxide no weighable quantity of the propylene glycol ether was obtained when propylene oxide was heated with N-p-cresol in the absence of alkali for two hours.

In the case of the more acidic phenols the effect of the presence of the free phenol is more important, as the following figures for ethylene oxide and $2:4:6$-trichlorophenol show:

Reaction solution.	Time of heating.	Yield of glycol trichlorophenyl ether. Per cent.	$k=\dfrac{1}{t}\log\dfrac{100}{100-x}.$
(i) N-Trichlorophenol ...	2 hours	2·0	—
(ii) N-Trichlorophenol $N/20$-Na· }	2 ,,	29·4	0·075
	4 ,,	48·1	0·071
	4 ,,	51·2	0·078
			Mean 0·075

In this case the velocity-constant calculated for the sodium salt is too high. The corrected constant for sodium trichlorophenoxide, taking into account the effect of the free trichlorophenol, would be approximately 0·071. As this correction, however, does not affect the main results of the investigation, the uncorrected results only are given in the table on p. 2123.

Another factor which affects the values of the observed velocity-constants is the action of the olefine oxide on the alcohol used as a solvent. It is probable that olefine oxides react slowly with ethyl alcohol, and more rapidly with sodium ethoxide, to form glycol ethyl ethers:

$$\begin{array}{c}CH_2\\|\\CH_2\end{array}\!\!>\!O + C_2H_5\cdot OH = CH_2(OH)\cdot CH_2\cdot O\cdot C_2H_5.$$
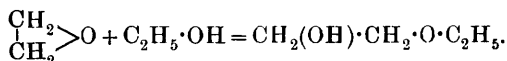
Owing, however, to the solubility in water of the products of this reaction in the case of ethylene or propylene oxide, the occurrence of this subsidiary reaction does not prevent the approximate estimation of the yield of glycol aryl ether by the method we have adopted. It has the effect, however, of slightly diminishing the values of the velocity-constants obtained for the sodium phenoxides. The magnitude of the effect so produced can be estimated from a consideration of the speed of combination of the olefine oxide and alcohol, and this can be determined approximately by measuring the maximum yields of glycol aryl ethers obtained in the case of the more acidic phenols, when the solutions remain neutral throughout the whole experiment.

The following data refer to ethylene oxide:

Reaction solution.	Yield in 2 hours. Per cent.	Maximum yield. Per cent.
N-p-Nitrophenol $N/20$-Na· } ...	5·6	74
N-m-Nitrophenol $N/20$-Na· } ...	13·4	87

Since a large excess of alcohol is present during the whole experiment, the reaction between the alcohol and the ethylene oxide may be regarded as a unimolecular one, and hence the ratio of the speeds of the two concurrent reactions, combination with alcohol, and combination with the sodium derivative of p-nitrophenol, may be taken as 26/74. Consequently, in the case of the p-nitrophenol solution we obtain for the percentage of ethylene oxide lost in two hours by combination with alcohol, $26/74 \times 5.6 = 2$ approximately. The figures in the case of m-nitrophenol give a similar result. Hence in the case of phenols sufficiently reactive for the experiments to be completed in two or four hours it has not been thought necessary to make any correction for this factor.

The yield of glycol aryl ether in two or four hours with some phenols, however, is so small that experiments were made involving longer periods.

In such cases the correction becomes important, as is shown by the following figures:

Time in hours.	Yield. Per cent.	k uncorrected.	k corrected.
N-o-Nitrophenol, $N/20$-Na$\cdot$, and ethylene oxide.			
2	3.3	0.0073	0.00736
46	47.5	0.0061	0.00740
N-p-Hydroxybenzonitrile, $N/20$-Na$\cdot$, and propylene oxide.			
2	6.69	0.0150	0.0152
11	29.6	0.0138	0.0144
N-Salicylonitrile, $N/20$-Na$\cdot$, and propylene oxide.			
2	8.49	0.0193	0.0195
15	45.0	0.0173	0.0192

The formula used for correction of the velocity-constant is as follows:

$$K = \frac{Y}{100}\left\{\frac{1}{t}\log\frac{1}{1-\dfrac{x}{Y}}\right\}^{*},$$

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* Let K = velocity-constant of formation of aryl ether.

,, $K^{\cdot}$ = ,, ,, ,, ethyl ether.

,, x = percentage of ethylene oxide transformed into aryl ether in t hours.

,, x^{1} = ,, ,, ,, ,, ethyl ,, ,,

,, Y = maximum percentage yield of aryl ether.

Then $x + x^{1}$ = total percentage of ethylene oxide transformed in t hours.

Hence
$$K + K^{1} = \frac{1}{t}\log\frac{100}{100 - (x + x^{1})}.$$

But $\dfrac{x}{x + x^{1}} = \dfrac{Y}{100}.$ $\therefore$ $x + x^{1} = \dfrac{100x}{Y}.$
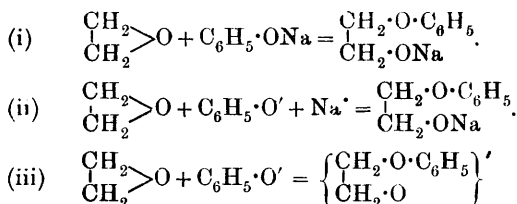
$$\therefore\ K + K^{1} = \frac{1}{t}\log\frac{100}{100 - \dfrac{100x}{Y}}$$

where K is the corrected velocity-constant for the reaction between the olefine oxide and the sodium phenoxide, x is the percentage yield in t hours, and Y is the maximum yield per cent.

This formula is based on the assumption that the reactions between the olefine oxide and the alcohol and sodium phenoxide respectively may both be regarded as unimolecular.

With regard to the mechanism of the reaction between the olefine oxide and the sodium phenoxide, three possibilities present themselves.

The reaction may occur (i) between the oxide molecule and the undissociated sodium phenoxide, or (ii) between the oxide molecule and the sodium and phenoxy-ions, or (iii) it may consist in the combination of the oxide molecule with the phenoxy-ion only, a new ion being formed. This would then react with the excess of phenol to give the undissociated glycol ether:

$$\text{(i)} \qquad \begin{matrix}\text{CH}_2\\|\\\text{CH}_2\end{matrix}\!\!>\!\!\text{O} + \text{C}_6\text{H}_5\text{·ONa} = \begin{matrix}\text{CH}_2\text{·O·C}_6\text{H}_5\\|\\\text{CH}_2\text{·ONa}\end{matrix}.$$

$$\text{(ii)} \qquad \begin{matrix}\text{CH}_2\\|\\\text{CH}_2\end{matrix}\!\!>\!\!\text{O} + \text{C}_6\text{H}_5\text{·O'} + \text{Na}^{\boldsymbol{\cdot}} = \begin{matrix}\text{CH}_2\text{·O·C}_6\text{H}_5\\|\\\text{CH}_2\text{·ONa}\end{matrix}.$$

$$\text{(iii)} \qquad \begin{matrix}\text{CH}_2\\|\\\text{CH}_2\end{matrix}\!\!>\!\!\text{O} + \text{C}_6\text{H}_5\text{·O'} = \left\{\begin{matrix}\text{CH}_2\text{·O·C}_6\text{H}_5\\|\\\text{CH}_2\text{·O}\end{matrix}\right\}'$$

As far as our experiments admit of a conclusion being drawn with regard to this question, it would appear that the third hypothesis is the most probable one. This is shown by the following considerations.

The effect on the velocity of reaction produced by an alteration in the concentration of the sodium phenoxide must evidently be different in the three cases. If, for example, the concentration of the sodium phenoxide were reduced from $N/20$ to $N/40$, then, owing to the increase in the degree of dissociation resulting from the dilution, the active mass of undissociated sodium phenoxide would be reduced to less than one-half of its previous value; hence, assuming equation (i) to represent the mechanism of the reaction, a diminution of the speed of the reaction to less than one-half of its previous value must follow.

$$= \frac{1}{t}\log\frac{1}{1-\dfrac{x}{Y}}$$

And
$$\frac{K}{K+K^1} = \frac{Y}{100}. \qquad \therefore\ K = \frac{Y}{100}(K+K^1).$$

$$\therefore\ K = \frac{Y}{100}\left(\frac{1}{t}\log\frac{1}{1-\dfrac{x}{Y}}\right).$$

In the case represented by equation (ii), halving the concentration of the sodium phenoxide would result in a reduction of the speed of the reaction to one-quarter of its former value, supposing the degree of dissociation were unaltered.   The increase in the degree of dissociation which accompanies the dilution would prevent the reduction in speed being quite so great, but the total result must be again a diminution in speed to less than one-half.   On the other hand, in the case represented by equation (iii) a diminution in the concentration of the sodium phenoxide from $N/20$ to $N/40$ would result in a diminution in the speed of the reaction to a value greater than one-half the original one, for the increase in the degree of dissociation will counterbalance, to some extent, the diminution in concentration of the phenolic salt.

Experiments with p-cresol and ethylene oxide gave the following results:

Reaction solution.	Time.	Yield. Per cent.	k.	Mean k.
(i) N-p-Cresol $N/20$-Na˙ $\Big\}\ldots$	1 hour	47·0	0·276	
	2 hours	71·8	0·275	0·279
	2 ,,	73·2	0·286	
(ii) N-p-Cresol $N/40$-Na˙ $\Big\}\ldots$	2 ,,	48·9	0·146	
	2 ,,	52·5	0·162	0·157
	4 ,,	77·6	0·163	

These facts are in harmony with the view of the reaction represented by equation (iii).

Summary of Results.

The following table contains the results of experiments carried out at 70·4° with N-phenol, $N/20$-Na˙ alcoholic solutions.   The velocity-constants given are mean values calculated on the results of at least two experiments of different periods of duration.   The experimental error varies somewhat with different phenols, but the figures already quoted for p-cresol, $2:4:6$-trichlorophenol, o-nitrophenol, p-hydroxybenzonitrile, and salicylonitrile may be taken as typical of the results obtained generally.

In a number of cases two or more experiments of the same period of duration were carried out, and in the column headed "Yield in two hours" the limits obtained in separate experiments of two hours' duration are given, the number of experiments carried out being indicated by the figure in brackets.

No.	Phenol.	Ethylene oxide.			Propylene oxide.		
		Yield in 2 hours. Per cent.	Maximum yield. Per cent.	$k = \frac{1}{t}\log\frac{100}{100-x}$	Yield in 2 hours. Per cent.	Maximum yield. Per cent.	$k = \frac{1}{t}\log\frac{100}{100-x}$
1.	ψ-Cumenol ...	78·9	94·2	0·338	44·8	89·6	0·125
2.	Thymol	74·9	90·7	0·311	39·9—38·5 (3)	90·6	0·107
3.	m-Dimethyl-aminophenol	*	*	*	38·9	92·6	0·105
4.	p-Cresol	73·2—71·8 (2)	97·0	0·279	38·5—36·3 (3)	92·5	0·101
5.	Carvacrol ...	68·8	92·9	0·257	38·8	89·8	0·101
6.	m-Cresol	69·8—68·1 (2)	98·0	0·256	32·1—31·8	90·9	0·083
7.	p-Xylenol ...	67·8	91·9	0·244	†	88·9	0·092
8.	Eugenol	65·6—62·8 (2)	96·0	0·226	32·0	95·8	0·080
9.	o-Cresol	64·5—64·1 (2)	94·5	0·225	30·8—28·9 (2)	94·1	0·078
10.	Phenol.........	60·8—60·3 (2)	96·7	0·205	30·1—28·5 (3)	92·7	0·075
11.	a-Naphthol .	54·9	97·5	0·173	30·9	97·9	0·083
12.	Guaiacol ...	53·7	99·3	0·171	26·2	91·6	0·064
13.	β-Naphthol .	48·7—48·3 (2)	95·1	0·144	22·5—21·1	94·2	0·053
14.	p-Chloro-phenol	40·6—38·3 (2)	95·5	0·108	17·7—16·8	92·9	0·042
15.	o-Chloro-phenol	39·0—38·6(2)	95·9	0·104	21·0—19·7 (2)	96·1	0·050
16.	m-Chloro-phenol	37·5—36·8(2)	95·7	0·101	17·9	92·0	0·043
17.	2 : 4 : 6-Tri-bromophenol	38·6—37·6 (3)	93·9	0·099	26·9—25·8 (3)	90·8	0·065
18.	2 : 4 : 6-Tri-chlorophenol	29·4	92·7	0·075	19·4—18·8 (3)	92·2	0·045
19.	p-Benzene-azophenol	20·9	90·7	0·050	10·2	86·0	0·023
20.	m-Hydroxy-benzonitrile	19·1	90·5	0·044	9·99	86·8	0·0224
21.	Salicylonitrile	14·3	81·9	0·033	8·49	79·5	0·0193
22.	m-Nitrophenol	13·4	87·2	0·032	6·73	85·0	0·0152
23.	p-Hydroxy-benzonitrile	11·1	81·6	0·026	6·69	81·4	0·0150
24.	p-Nitrophenol	5·6	73·6	0·013	3·2—3·14 (2)	71·6	0·0075
25.	o-Nitrophenol	3·3	71·1	0·0073	2·38	73·4	0·0035

* Owing to the solubility in water of glycol m-dimethylaminophenyl ether it was not found possible to estimate the yield in the case of ethylene oxide.

† The velocity-constant was calculated from experiments of one, three, and four hours' duration. The percentage yield in three hours was 47·0.

Below are given the results of a few experiments carried out with N-phenol solutions and ethylene oxide in the absence of alkali :

Phenol.	Time, in hours.	Yield. Per cent.	$k = \frac{1}{t}\frac{x}{100(100-x)}$
Thymol	24	7·14	32×10^{-6}
p-Cresol	2	1·01	51
2 : 4 : 6-Tribromophenol	2	2·7	139
2 : 4 : 6-Trichlorophenol	2	2·0	102
p-Nitrophenol	2	0·43	22
o-Nitrophenol	2	0·14	7

Conclusions.

Directing attention in the first place to the results obtained in the case of ethylene oxide, the following conclusions may be drawn:

(1) The reactivity of the sodium phenoxide is enhanced by the presence of positive groups, for example, $\cdot CH_3$, $\cdot C_3H_7$,

$$\cdot CH_2 \cdot CH:CH_2,$$

and diminished by the presence of negative groups, for example, $\cdot OMe$, $\cdot CH:CH \cdot CH:CH \cdot$, $\cdot Cl$, $\cdot Br$, $C_6H_5 \cdot N:N \cdot$, $\cdot CN$, $\cdot NO_2$.

(2) Broadly speaking, it may be said that the speed of the reaction between ethylene oxide and the sodium phenoxide diminishes with increase in the acidity of the phenol. Exact data with regard to the relative acidities of the majority of phenols are, unfortunately, not available.

The following figures, however, bring out the general correctness of the foregoing statement:

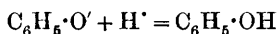| Phenol.	Hydrolysis of sodium salt at 25° V_{32} (Hantzsch and Farmer).* Per cent.	Velocity-constant of combination of sodium salt and ethylene oxide at 70·4°.
Phenol	6·0	0·205
p-Chlorophenol	2·88	0·108
o-Chlorophenol	2·1	0·104
p-Hydroxybenzonitrile	0·52	0·026
$2:4:6$-Trichlorophenol	0·37	0·075
p-Benzeneazophenol	0·33	0·05
p-Nitrophenol	0·28	0·012

* *Ber.*, 1899, **32**, 3066, 3089.

Of the seven phenols mentioned in the above list, five show a remarkably close agreement as regards the reactivity of the sodium salt towards ethylene oxide on the one hand and its tendency towards hydrolysis in aqueous solution on the other. The two exceptions are p-benzeneazophenol and $2:4:6$-trichlorophenol. With regard to the former it is to be noticed that, as Hantzsch and Farmer point out, the method employed by them to determine the percentage of hydrolysis of the sodium salt, namely, hydrolysis of methyl acetate, is unsatisfactory in the case of this particular phenol, owing to its insolubility in water. A subsequent determination of the percentage of hydrolysis of the barium salt by Farmer by a different method (T., 1901, **79**, 864) gave 0·90 at V_{32} and 25°, a result which agrees well with the value found for the reactivity of the sodium salt towards ethylene oxide. $2:4:6$-Trichlorophenol, on the other hand, stands out as a remarkable exception to the rule, the reactivity of its sodium salt towards ethylene oxide being five or six times as great as would be expected from the extent of its hydrolysis in aqueous solution.

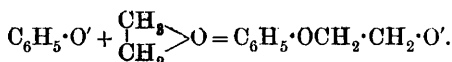This relationship between the speed of reaction of ethylene oxide

with the sodium derivative of a phenol and the acidity of the phenol finds a plausible explanation in the view already expressed that the process consists essentially in a combination of the olefine oxide with the phenoxy-ion:

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!\!O + C_6H_5 \cdot O' = \left\{ \begin{matrix} CH_2 \cdot O \cdot C_6H_5 \\ | \\ CH_2 \cdot O \end{matrix} \right\}$$
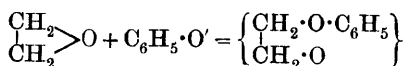
Pronounced acidity on the part of a phenol implies a comparatively small tendency on the part of the phenoxy-ion to form an additive compound with a hydrogen ion; that is to say, it implies a considerable capacity on the part of the phenoxy-ion for stable independent existence in a suitable solvent. The p-cyanophenoxy-ion, to take one example, must be essentially a more stable grouping than the simple unsubstituted phenoxy-ion; and it seems not unreasonable to suppose that this stability would be exhibited, not only in relation to the hydrogen ion, but also in respect to other possible additive reactions, for instance, combination with an ethylene oxide molecule. In any case the facts appear to indicate that a certain analogy does exist between the two reactions:

$$C_6H_5 \cdot O' + H^{\cdot} = C_6H_5 \cdot OH$$

and

$$C_6H_5 \cdot O' + \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!\!O = C_6H_5 \cdot OCH_2 \cdot CH_2 \cdot O'.$$

(3) The reactivity of the sodium phenoxide depends on the positions of the substituent groups or atoms, as well as on their chemical nature; thus, thymol is considerably more reactive than the isomeric carvacrol, p-cresol than o-cresol. It is not possible, however, in the case of mono-substituted phenols to recognise any general rule connecting the position of a substituent and the magnitude of its effect on the reactivity of the sodium salt. In the four different o-, m-, and p-series which we have investigated, the order of reactivity is different in each case:

Cresols.	k.	Chloro-phenols.	k.	Hydroxy-benzo-nitriles.	k.	Nitro-phenols.	k.
p-	0·28	p-	0·108	m-	0·044	m-	0·032
m-	0·26	o-	0·104	o-	0·033	p-	0·012
o-	0·23	m-	0·101	p-	0·026	o-	0·0073

(4) The velocity-constants of $2:4:6$-trichloro- and $2:4:6$-tribromo-phenol give no indication of steric hindrance in the case of these phenols.

It would even appear from a consideration of the abnormal reactivity of sodium trichlorophenoxide already referred to, that two ortho-placed substituents, instead of hindering the combination

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of the phenoxy-ion with the ethylene oxide molecule, actually favour it in some special way.

Turning now to the data in the case of propylene oxide, the following additional points may be noted :

(5) The speed of reaction between a sodium phenoxide and propylene oxide is always much lower than the speed of reaction between the same sodium phenoxide and ethylene oxide.   In the case of phenol we have :

$$\frac{\text{Velocity constant for ethylene oxide}}{\text{Velocity constant for propylene oxide}} \; = \; \frac{0\cdot075}{0\cdot205} \; = \; 0\cdot37,$$

and the ratio has approximately the same value for the majority of the less acidic phenols.

In the case of the more acidic phenols it has a higher value; for p-nitrophenol $0\cdot58$, for m-hydroxybenzonitrile $0\cdot51$.   The highest value, $0\cdot66$, is reached in the case of $2:4:6$-tribromophenol.

(6) The phenols stand, as regards the reactivity of their sodium salts, in almost the same order in the case of propylene oxide as in the case of ethylene oxide.   The most notable exceptions are the trichloro- and tribromo-phenols, α-naphthol and o-chlorophenol. These four phenols, two of which are ortho-substituted and the other two diortho-substituted, are much more reactive towards propylene oxide than would be expected from a consideration of the results obtained for the same phenols in the case of ethylene oxide.   This is the more remarkable since in the case of ortho- and more especially in that of diortho-substituted phenols one might have anticipated a special retardation of the velocity as the result of the steric influence of the methyl group.   Experiment shows, however, that precisely the opposite is the case.   Instead of the reaction of the propylene oxide being retarded relatively to that of the ethylene oxide by the presence in a phenol of two ortho-substituents, it appears actually to be accelerated by the presence of these substituents.

(7) Very striking evidence in favour of the view that two ortho-placed substituents exert an accelerating influence on the reaction between olefine oxides and sodium phenoxides is found in the propylene oxide data for p-chlorophenol and $2:4:6$-trichlorophenol.   In spite of the much greater acidity of the trichlorophenol, its velocity-constant is as great as, if not greater than, that of p-chlorophenol.

(8) With regard to the results of the experiments in which ethylene oxide was heated with free phenols, it may be remarked that they show a qualitative agreement with the view that the formation of the glycol aryl ether depends on the combination of the ethylene oxide molecule with the phenoxy-ion.   Thus, although,

as shown by the experiments with sodium phenoxides, the
p-tolyloxy-ion is much more reactive than the trichlorophenoxy-
ion, nevertheless, owing to the concentration of ions being much
greater in the solution of free trichlorophenol than in that of
p-cresol, the actual speed of formation of glycol aryl ether in the
absence of alkali is greater in the case of trichlorophenol than in
that of p-cresol.

The velocity-constants of the free o- and p-nitrophenols also
approach that of free p-cresol much more nearly than the constants
for the sodium derivatives of the nitrophenols do that of sodium
p-tolyloxide, as would be expected from the fact that the disso-
ciation constants of the nitrophenols are greater than that of
p-cresol.

(9) The experiments with benzeneazophenol show that the
product obtained by the action of ethylene oxide on the sodium salt
of this phenol is the same substance as is produced by the action
of ethylene oxide on the free azophenol. This observation gives
support to the view that the free azo-compound is present in aqueous
alcoholic solution mainly, if not entirely, as a hydroxy-compound,
and not to any considerable extent in the form of a quinone-
hydrazone.

Comparison of Results with those of Previous Investigations.

Several investigations have in recent years been carried out with
the object of determining the influence of substituents on the
reactivities of phenols.

Schryver (T., 1899, **75**, 661) investigated the behaviour of the
sodium salts of a number of phenols towards the anhydride of
camphoric acid, and found that in the majority of cases reaction
takes place readily between the solid sodium salt and the camphoric
anhydride dissolved in xylene, in accordance with the equation:
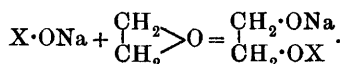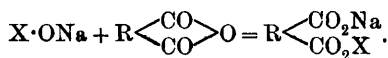
$$XONa + R{<}^{CO}_{CO}{>}O = R{<}^{CO_2Na}_{CO_2X}.$$
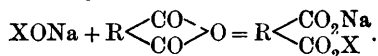
Two classes of substituted phenols proved, however, to be incap-
able of reacting with camphoric anhydride under the conditions
employed by Schryver, namely, o- and p-nitrophenols and di-o-
bromophenols.

Although the sodium salt of m-nitrophenol reacts with a xylene
solution of camphoric anhydride fairly readily at water-bath tem-
perature, no reaction could be brought about between camphoric
anhydride and the sodium salts of o- and p-nitrophenols, even on
prolonged heating at 180°. Again, although reaction occurred
readily between the xylene solution of camphoric anhydride and
the sodium salts of 4-bromo- and 2:4-dibromo-phenol, no reaction

could be brought about between the camphoric anhydride solution
and the sodium salts of 2:6-dibromo- and 2:4:6-tribromo-phenol
even when the mixtures were heated in sealed tubes at 150—180°.

These results of Schryver with regard to *o*- and *p*-nitrophenols
and the diortho-substituted phenols offer a remarkable contrast to
our observations, a fact which is the more interesting since the two
reactions appear at first sight to be distinctly similar in character:

$$X \cdot ONa + R \left\langle {}^{CO}_{CO} \right\rangle O = R \left\langle {}^{CO_2Na}_{CO_2X} \right. .$$

$$X \cdot ONa + {}^{CH_2}_{CH_2} \!\!\!\! \left. \right\rangle O = {}^{CH_2 \cdot ONa}_{CH_2 \cdot OX} .$$

It is to be noted, however, that whilst our experiments were
carried out in alcoholic solution with the result that the reaction
probably took place mainly, if not exclusively, between the phenoxy-
ion and the olefine oxide molecule, in Schryver's experiments a
solution of camphoric anhydride in xylene was allowed to act on
the solid sodium salt of the phenol, and the reaction was probably
limited almost entirely to the undissociated phenolic salt.   More-
over, under the conditions employed by Schryver an important
factor in determining the speed of reaction must necessarily be
the solubility of the sodium salt in xylene, and it appears not
impossible that this factor may have had some influence in produc-
ing the phenomena observed by him.

In the somewhat analogous case of the action of aqueous
hydriodic acid on phenolic ethers it was found by Boyd and Pitman
(T., 1905, **87**, 1255) that 2:4:6-trichloro- and 2:4:6-tribromo-
anisole showed an exceptional stability towards this reagent; but
this stability is due in all probability merely to the insolubility of
these ethers in the reagent, since it disappears when the hydriodic
acid is allowed to act on them in a medium in which the ethers are
soluble.

This solubility factor, unfortunately, also throws obscurity upon
the meaning to be attached to the results obtained by Bischoff
(*Ber.*, 1900, **33**, 1249) in an investigation of the action of the
sodium salts of various phenols on α-bromopropionic, α-bromo-
butyric, α-bromo*iso*butyric, and α-bromo*iso*valeric esters.

The method of experiment consisted in boiling the sodium salt
of the phenol with a solution of the bromo-ester in light petroleum
for one hour, and determining the yield of phenoxy-derivative.
Some of Bischoff's results differ to a remarkable extent from ours,
as is shown by the following figures:

Phenol.	Yield of propionic ester derivative in one hour at 65—70°. Per cent.	Yield of ethylene oxide derivative in two hours at 70·4°. Per cent.
Thymol	98	75
o-Cresol	95	64
Phenol	92	61
p-Cresol	62	72
p-Xylenol	59	68
ψ-Cumenol ...	44	79
Guaiacol	40	54
p-Nitrophenol	0	5·6

Thus, whereas we find it to be an invariable rule that the intro-
duction of one or more alkyl groups increases the reactivity of
phenol, in several of Bischoff's experiments the reactivity of the
alkyl-substituted phenol is less than that of phenol itself. Parti-
cularly striking is the case of ψ-cumenol, which Bischoff finds to be
the least reactive of all the alkyl-substituted phenols investigated
by him, but which we find to be the most reactive. It is, of course,
the case that the reaction investigated by Bischoff is a double
decomposition, whilst that studied by us is an additive reaction.
Even this difference of character, however, would hardly have been
expected to produce such entirely opposite results. Bischoff's
observations on the retarding influence of negative groups, parti-
cularly nitro-groups, agree with our own.

Similar observations on the retarding influence of negative
groups were made by Auwers and Haymann (Ber., 1894, 27, 2795),
who studied the action of ethyl chloroacetate in alcoholic solution
on the sodium salts of certain phenols. Auwers and Haymann
found, for example, that no reaction took place on digesting the
sodium salts of o- and p-nitrophenol for thirty hours on a water-
bath with an alcoholic solution of ethyl chloroacetate. The latter
reaction has been re-investigated recently by Hewitt, Johnson, and
Pope (T., 1913, 103, 1626). These authors obtained a fair yield
of ethyl m-nitrophenoxyacetate by the action of ethyl chloroacetate
in absolute alcoholic solution at water-bath temperature on the
sodium salt of m-nitrophenol, but they were unable to isolate the
isomeric ethyl o- and p-nitrophenoxyacetates after treating the
sodium salts of o- and p-nitrophenol in a similar way. From this
result they draw the conclusion that in the sodium salts of o- and
p-nitrophenol the grouping $:C \cdot ONa$ is wanting.

Our experiments, however, which show a steady gradation in the
reactivities of the three nitrophenols, lend no support to the view
that the sodium salts of o- and p-nitrophenol differ in constitution
from the sodium salt of m-nitrophenol. The velocity-constants of
reaction with ethylene oxide for the sodium salts of phenol and the
three nitrophenols are as follows:

Phenol, 0·21; *m*-nitrophenol, 0·032; *p*-nitrophenol, 0·012; *o*-nitrophenol, 0·007.

The introduction of the ·NO_2 group in the meta-position thus lowers the reactivity of phenol to about 1/7 of its value; the same group in the para-position reduces the reactivity to about 1/17, and in the ortho-position to about 1/30. Such differences are not greater than might naturally arise from the differences in the position of the ·NO_2 group in the benzene nucleus.

Our results, of course, do not preclude the possibility that all three nitrophenols give rise to nitronic salts, $O{:}C_6H_4{:}N{<}^O_{ONa}$, and that these react with the olefine oxides to produce nitronic esters which are quickly transformed into the more stable phenolic ethers.

EXPERIMENTAL.

As regards the method employed for the estimation of the glycol aryl ethers, one or two points in addition to those already mentioned on p. 2117 may be indicated.

In order to prevent any possibility of alcohol vapour catching fire during the process of sealing the reaction tube and so introducing carbon dioxide which would cause the precipitation of sodium carbonate, it was found advantageous to displace the air in the tube by means of nitrogen. It was found useful also to place in the reaction tube a small piece of glass rod, as this rendered the breaking of the bulb containing the olefine oxide much easier.

For the removal of the excess of phenol remaining after the reaction was over, a roughly normal solution of potassium hydroxide was employed.

In the majority of cases it was found necessary to shake seven or eight times with potassium hydroxide solution in order to remove the phenol completely. In certain cases, namely, those of thymol, carvacrol, *p*-xylenol, and *ψ*-cumenol, it was found impossible to extract all the free phenol by shaking an ethereal solution with aqueous potassium hydroxide.

The difficulty, however, was overcome by employing light petroleum (b. p. below 50°) as the solvent for the glycol aryl ether, the excess of the phenol being then removed by six or eight shakings with aqueous potassium hydroxide. In order to prevent loss of glycol aryl ether in the aqueous solution, it was necessary to shake the series of alkaline liquors several times with fresh quantities of ether, or light petroleum, as the case might be. From 50 to 100 c.c. of ether were employed in the first extraction, and three or four portions, each of 50 c.c., in extracting the alkaline liquors, whilst

about 30 c.c. of aqueous potassium hydroxide were used in each washing. In commencing experiments with a new phenol, the last portion of ether was always evaporated separately, in order to ascertain if the extraction of the glycol aryl ether had been approximately complete. The following was found to be a convenient test for proving that the excess of phenol had been completely removed from the ethereal solution. Two or three c.c. of the last washing liquor were boiled to remove dissolved ether, then mixed with an equal volume of concentrated nitric acid, and boiled again for a few minutes. The liquid after cooling was mixed with excess of sodium hydroxide, when the solution acquired a brownish-yellow colour if phenol were present.

The greater part of the solvent used in extraction was evaporated in a water-bath, but in order to prevent possible loss of glycol ether by vaporisation, the last few c.c. were removed in a current of air.

Some of the glycol aryl ethers are hygroscopic, and, when oils, they were found to retain persistently small quantities of the solvent ether. Hence it was sometimes necessary to dry in a vacuum desiccator over sulphuric acid for several days before the weight became constant. In a few cases it was found that appreciable vaporisation takes place in a vacuum, and a constant loss of 1 to 3 milligrams in twenty-four hours was observed. In estimating the yields in these cases an allowance was made corresponding with the number of days during which the glycol ether had been drying, and the constant loss observed.

The majority of the aryl ethers obtained from ethylene oxide were crystalline substances, and of a high degree of purity, as was shown by analysis. The oily ethylene glycol ethers all readily gave crystalline p-nitrobenzoates, the purity of which was also ascertained by analysis.

The derivatives of propylene oxide, on the other hand, were, in the majority of cases, oils at the ordinary temperature, and in all cases appeared to consist of two compounds. The explanation of this fact is suggested by the following formulæ:

$$CH_3 \cdot CH(OH) \cdot CH_2 \cdot OR \quad \text{and} \quad CH_3 \cdot CH(OR) \cdot CH_2 \cdot OH.$$
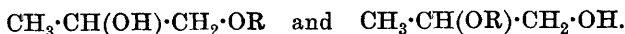
The quantities of the propylene glycol ethers prepared were small, and in no case enough to effect a complete separation of either constituent in sufficient amount to permit of a decision as to which of the two isomerides had been separated. In a few cases, however, one constituent proved to be so sparingly soluble in light petroleum that the other could be obtained in a state of purity by recrystallisation.

Usually a mixture of the two isomerides was analysed after one or two crystallisations, and the results of the analyses indicate that

the product of the action of propylene oxide on a sodium phenoxide consists entirely of substances having the empirical formula $C_3H_6O_2R$, in agreement with the view that a mixture of compounds having the above formula is in question.

In the case of propylene glycol $2:4:6$-tribromophenyl ether a complete separation was effected. After repeated crystallisation from light petroleum, followed by crystallisation from dilute alcohol, three fractions were obtained, melting at 78—79°, 64—65°, and 42·5—43·5° respectively. The first and third fractions gave analyses agreeing with the composition $C_9H_9O_2Br_3$, the second was not analysed. It would appear that the first two are probably the isomeric ethers, whilst the third, the most soluble, is a eutectic mixture of these.

In view of the uncertainty as to which of the two isomerides is in question in those cases in which fractions having a sharp melting point were obtained, only typical ethers were analysed, sufficient to prove that the reaction proceeds as indicated, and that the products have the above empirical composition corresponding with one or both of the constitutional formulæ given above.

The alcohol employed as solvent was commercial ethyl alcohol which had been boiled for some hours with solid sodium hydroxide and distilled. It had D_4^{25} 0·79058, corresponding with 98·1 per cent. of ethyl alcohol. The presence of 2 per cent. of water made it possible to obtain $N/20$-solutions of the sodium salts of the nitrophenols, which are only sparingly soluble in absolute alcohol.

The N-phenol, $N/20$-Na˙ solutions of the nitrophenols, were prepared in the reaction tubes by mixing standard solutions of the nitrophenols and sodium ethoxide in the proper proportions. In the case of o-nitrophenol a small quantity of the sodium salt separated at room temperature, but a clear solution was obtained at 70·4°. The N-phenol, $N/20$-Na˙ solution of benzeneazophenol was prepared at 35° instead of at room temperature.

The ethylene oxide, after redistillation, boiled at 12·5—13°/757 mm.

The propylene oxide was prepared from propylene glycol by first converting this into the chlorohydrin by the action of sulphur chloride. The crude product was fractionated ten or twelve times, and the resulting liquid, boiling at 127—129°, was cautiously treated with concentrated aqueous potassium hydroxide and distilled. The crude propylene oxide so obtained was allowed to remain over potassium carbonate, distilled, and left in contact with metallic sodium to remove the last traces of water, and then repeatedly fractionated.

The treatment with sodium appeared to be necessary, as distilla-

tion over other dehydrating agents was not sufficient to remove the water. Unfortunately, the yield of propylene oxide was very much reduced by this treatment. Several other methods of preparation were tried, but the yield was even less satisfactory, and the product less pure. The fraction boiling at 34—36° under atmospheric pressure was used in the experiments.

The purity of the phenols was controlled by melting-point or boiling-point determinations.

Experimental Data.

The following examples of the experimental data obtained are given in full for illustrative purposes:

Phenol.

Ethylene Oxide.						Propylene Oxide.				
Time, hours.	Oxide. Gram.	Ether. Grams.	Yield. Per cent.	k.		Time, hours.	Oxide. Gram.	Ether. Gram.	Yield. Per cent.	k.
2	0·414	0·783	60·3	0·201		2	0·332	0·247	28·5	0·073
2	0·414	0·790	60·8	0·203		2	0·427	0·336	30·1	0·078
4	0·517	1·389	85·7	0·211		2	0·182	0·138	28·9	0·074
117(∞)	0·160	0·486	96·7			4	0·192	0·247	49·2	0·074
						48(∞)	0·123	0·299	92·7	

Glycol phenyl ether p-*nitrobenzoate* was prepared by treating a solution of the ether in pyridine with p-nitrobenzoyl chloride, the method followed being that described by Henderson and Heilbron (P., 1913, **29**, 381). It crystallises from alcohol in needles melting at 63°.

In bulk the crystals showed a very pale yellow colour:

0·1961 gave 8·4 c.c. N_2 (moist) at 19° and 767 mm. N = 4·97.
$C_{15}H_{13}O_5N$ requires N = 4·88 per cent.

Glycol o-*tolyl ether*, $C_7H_7 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, is a colourless oil boiling at 141°/19 mm. The p-*nitrobenzoate* crystallised from alcohol in colourless, iridescent plates, melting at 78·5—79·5°:

0·2172 gave 8·8 c.c. N_2 (moist) at 16° and 771 mm. N = 4·79.
$C_{16}H_{15}O_5N$ requires N = 4·65 per cent.

The mixture of isomeric *propylene glycol* o-*tolyl ethers* formed a yellow oil. The p-*nitrobenzoates*, after crystallisation from alcohol, formed white, microscopic crystals, melting between 78° and 84°:

0·2308 gave 9·4 c.c. N_2 (moist) at 21° and 769 mm. N = 4·68.
$C_{17}H_{17}O_5N$ requires N = 4·45 per cent.

Glycol m-*tolyl ether* was obtained as a colourless oil boiling at 145—147°/19 mm. The p-*nitrobenzoate* crystallised from alcohol in clusters of minute, colourless plates, melting at 80·5—81·5°:

0·2006 gave 8·3 c.c. N_2 (moist) at 14° and 760 mm. $N=4·87$.

$\qquad$ $C_{16}H_{15}O_5N$ requires $N=4·65$ per cent.

Glycol p-*tolyl ether* crystallises from hot light petroleum in colourless prisms, melting at 44—45°:

0·1666 gave 0·4331 CO_2 and 0·1187 H_2O. $C=70·89$; $H=7·97$.

$\qquad$ $C_9H_{12}O_2$ requires $C=71·01$; $H=7·96$ per cent.

Glycol p-*xylyl ether*, $C_8H_9 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, crystallises from hot light petroleum (b. p. 40—65°) in clusters of fine needles melting at 46°:

0·1488 gave 0·3939 CO_2 and 0·1126 H_2O. $C=72·19$; $H=8·48$.

$\qquad$ $C_{10}H_{14}O_2$ requires $C=72·23$; $H=8·51$ per cent.

Glycol ψ-*cumyl ether*, $C_9H_{11} \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, crystallises from light petroleum in colourless, prismatic crystals, melting at 70—71°:

0·1390 gave 0·3736 CO_2 and 0·1116 H_2O. $C=73·28$; $H=9·00$.

$\qquad$ $C_{11}H_{16}O_2$ requires $C=73·24$; $H=8·97$ per cent.

Since this ether is not very readily soluble in cold light petroleum a mixture of light petroleum with a small quantity of ordinary ether was used as the extracting solvent in the experiments on the velocity of reaction.

Glycol 3-*methyl*-6-iso*propylphenyl ether*, $C_{10}H_{13} \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, remained as an almost colourless oil on evaporation of the light petroleum used as extracting solvent. Some months later it spontaneously crystallised on being poured from one vessel to another, forming a white, crystalline mass. It was dissolved in hot light petroleum (b. p. 68—73°), from which, on seeding the cold solution, it separated in transparent prisms melting at 53—54°:

0·2097 gave 0·5687 CO_2 and 0·1739 H_2O. $C=73·96$; $H=9·29$.

$\qquad$ $C_{12}H_{18}O_2$ requires $C=74·16$; $H=9·36$ per cent.

The mixture of isomeric *propylene glycol* 3-*methyl*-6-iso*propylphenyl ethers* formed a yellow, viscous oil. The p-*nitrobenzoates* formed a pasty mass completely soluble in light petroleum, from which crystals slowly separated on evaporation of the solvent. The crystals were drained from oil on a porous plate, and recrystallised from alcohol. In this way the less soluble isomeride was obtained in pale yellow crystals melting at 60·5—62°:

0·4570 gave 16·1 c.c. N_2 (moist) at 21° and 762 mm. $N=4·02$.

$\qquad$ $C_{20}H_{23}O_5N$ requires $N=3·92$ per cent.

Glycol 2-*methyl*-5-iso*propylphenyl ether*,

$$C_{10}H_{13} \cdot O \cdot CH_2 \cdot CH_2 \cdot OH,$$

separates from light petroleum (b. p. 40—60°) in silky needles melting at 51—52°:

0·1407 gave 0·3830 CO_2 and 0·1174 H_2O. $C = 74·25$; $H = 9·36$.

$C_{12}H_{18}O_2$ requires $C = 74·16$; $H = 9·36$ per cent.

Glycol o-methoxyphenyl ether, $CH_3 \cdot O \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, was obtained as a colourless oil boiling at 166—167°/22 mm.   On remaining it slowly changed to a mass of deliquescent, white crystals with a low melting point.   The p-*nitrobenzoate* separated from alcohol in rosettes of white crystals melting at 87—88°:

0·1919 gave 7·5 c.c. N_2 (moist) at 14° and 749 mm. $N = 4·53$.

$C_{16}H_{15}O_6N$ requires $N = 4·42$ per cent.

Glycol 2-methoxy-4-allylphenyl ether,

$$CH_3 \cdot O \cdot C_6H_3(C_3H_5) \cdot O \cdot CH_2 \cdot CH_2 \cdot OH,$$

dissolves very readily in ether, benzene, alcohol, or ethyl acetate. It was recrystallised by dissolving in dry ether and adding to the solution sufficient light petroleum to produce a slight turbidity. On cooling the turbid liquid in a freezing mixture, the substance separated quickly in colourless needles, melting at 36—37°:

0·1392 gave 0·3518 CO_2 and 0·0965 H_2O. $C = 68·93$; $H = 7·77$.

$C_{12}H_{16}O_3$ requires $C = 69·18$; $H = 7·76$ per cent.

Glycol α-naphthyl ether, $C_{10}H_7 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, was obtained as a red, crystalline mass.   It was purified from small quantities of colouring matter by extracting the crude product repeatedly with light petroleum.   On cooling the petroleum solution the glycol ether separated as an oil, which solidified on rubbing with a crystal. It was then dissolved in dry ether, in which it is very readily soluble, and to this solution light petroleum was added until a faint opalescence was produced.

A crystal of the glycol ether was then introduced, and the solution left for some time, when clusters of minute, colourless plates separated, which melted at 42°:

0·1450 gave 0·4054 CO_2 and 0·0836 H_2O. $C = 76·26$; $H = 6·46$.

$C_{12}H_{12}O_2$ requires $C = 76·56$; $H = 6·44$ per cent.

The mixture of isomeric *propylene glycol α-naphthyl ethers* formed an oil which slowly solidified to a mass of pink crystals. These were moderately soluble in boiling light petroleum, and from this solution one of the ethers separated as a woolly mass of needles melting at 64—65°, the other being left as an oil.

Glycol β-naphthyl ether was obtained as a crystalline solid with a slightly pink colour. It was recrystallised twice from hot benzene, from which it separated as an almost colourless, crystalline powder, melting at 76°:

0·1667 gave 0·4669 CO_2 and 0·0964 H_2O. $C = 76·38$; $H = 6·48$.

$C_{12}H_{12}O_2$ requires $C = 76·56$; $H = 6·44$ per cent.

The mixture of isomeric *propylene glycol β-naphthyl ethers* con-

sisted of pink crystals. Crystallisation from dilute alcohol, followed by crystallisation from light petroleum, gave a colourless fraction melting at 80—82°:

0·1290 gave 0·3629 CO_2 and 0·0825 H_2O. $C = 76·72$; $H = 7·16$.
$C_{13}H_{14}O_2$ requires $C = 77·19$; $H = 6·98$ per cent.

Glycol o-*chlorophenyl ether*, $C_6H_4Cl·O·CH_2·CH_2·OH$, was obtained as a colourless oil boiling at 159—161°/22 mm. The p-*nitrobenzoate* crystallises from alcohol in small, transparent plates, with a pale yellow tinge and melting at 81—82°:

0·1944 gave 7·3 c.c. N_2 (moist) at 18° and 768 mm. $N = 4·38$.
$C_{15}H_{12}O_5NCl$ requires $N = 4·36$ per cent.

Glycol m-*chlorophenyl ether* is a colourless oil boiling at 163—164°/22 mm. The p-*nitrobenzoate* crystallises from alcohol in small, dense crystals with a very pale yellow tint, and melting at 104°:

0·1672 gave 6·2 c.c. N_2 (moist) at 17° and 768 mm. $N = 4·35$.
$C_{15}H_{12}O_5NCl$ requires $N = 4·36$ per cent.

The mixture of isomeric *propylene glycol* m-*chlorophenyl ethers* formed an oily liquid. The p-*nitrobenzoates*, after repeated crystallisation from light petroleum and from alcohol, were partly separated. The specimen analysed melted at 98·5—101°:

0·2129 gave 8·1 c.c. N_2 (moist) at 15° and 738 mm. $N = 4·33$.
$C_{16}H_{14}O_5NCl$ requires $N = 4·18$ per cent.

Glycol p-*chlorophenyl ether* was obtained as an almost colourless, crystalline mass, melting at about 28°. The p-*nitrobenzoate* crystallises from alcohol in needles with a very pale yellow tinge, and melting at 90—91°:

0·1729 gave 6·5 c.c. N_2 (moist) at 18° and 766 mm. $N = 4·38$.
$C_{15}H_{12}O_5NCl$ requires $N = 4·36$ per cent.

The *glycol* 2:4:6-*trichlorophenyl ether*,

$$C_6H_2Cl_3·O·CH_2·CH_2·OH,$$

was crystallised from hot light petroleum (b. p. 68—75°), from which it separates in prismatic needles melting at 77°:

0·1946 gave 0·3471 AgCl. $Cl = 44·13$.
$C_8H_7O_2Cl_3$ requires $Cl = 44·08$ per cent.

Glycol 2:4:6-*tribromophenyl ether*, $C_6H_2Br_3·O·CH_2·CH_2·OH$, crystallises from hot ethyl alcohol in fine needles melting at 116°:

0·1710 gave 0·2583 AgBr. $Br = 64·27$.
$C_8H_7O_2Br_3$ requires $Br = 63·97$ per cent.

The mixture of isomeric *propylene glycol* 2:4:6-*tribromophenyl ethers* by repeated crystallisation, first from light petroleum and afterwards from dilute alcohol, was separated into three fractions

melting at 78—79°, 64—65°, and 42·5—43·5° respectively. The first and third fractions were analysed:

I. 0·0867 gave 0·1263 AgBr. Br = 61·96.

III. 0·1402 ,, 0·2031 AgBr. Br = 61·64.

$C_9H_9O_2Br_3$ requires Br = 61·67 per cent.

Glycol p-*benzeneazophenyl ether*, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, crystallises from benzene in orange-coloured needles melting at 100°:

0·1231 gave 12·4 c.c. N_2 (moist) at 14° and 759 mm. N = 11·84.

$C_{14}H_{14}O_2N_2$ requires N = 11·57 per cent.

In order to ascertain whether benzeneazophenol, in the absence of alkali, would react with ethylene oxide as a quinone-hydrazone, producing a derivative of the formula

$$C_6H_5 \cdot N(CH_2 \cdot CH_2 \cdot OH) \cdot N\!:\!C_6H_4\!:\!O,$$
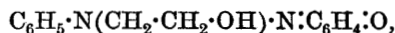
a solution of the free phenol was heated with ethylene oxide for some hours. Since it has been shown by Knorr (*Ber.*, 1899, **32**, 729) that ethylene oxide does not react easily with amines in the absence of water, the solvent employed in this case was a mixture of alcohol and water in about equal proportions by volume. The product under these conditions was quite similar in appearance to the substance produced when alkali was present, and had the same melting point. A mixture of the two products in about equal proportions also melted at the same temperature.

It would appear, therefore, that the same substance, namely, that of the formula $C_6H_5 \cdot N\!:\!N \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, was produced in each case.

The mixture of isomeric *propylene glycol benzeneazophenyl ethers* consisted of orange crystals, sparingly soluble in light petroleum. This solvent readily effects a separation of the two ethers, the more soluble isomeride crystallising with difficulty. The specimen analysed melted at 99—101·5°:

0·1970 gave 18·3 c.c. N_2 (moist) at 12° and 751 mm. N = 10·86.

$C_{15}H_{16}O_2N_2$ requires N = 10·94 per cent.

Glycol o-*cyanophenyl ether*, $CN \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, was obtained as a colourless oil boiling at 203°/19 mm. The p-*nitrobenzoate* separates from alcohol in almost colourless, minute, prismatic crystals, melting at 108°:

0·1913 gave 14·7 c.c. N_2 (moist) at 16° and 766 mm. N = 9·03.

$C_{16}H_{12}O_5N_2$ requires N = 8·98 per cent.

Glycol m-*cyanophenyl ether* was crystallised by dissolving it in pure dry ether, and adding to the solution sufficient light petroleum to produce an opalescence. The glycol ether separated slowly in colourless, microscopic crystals, melting at 52—53°:

0·1467 gave 10·7 c.c. N_2 (moist) at 12° and 760 mm. $N = 8·66$.
$C_9H_9O_2N$ requires $N = 8·59$ per cent.

Glycol p-*cyanophenyl ether* crystallises from benzene in prismatic needles, melting at 86°:

0·1437 gave 10·6 c.c. N_2 (moist) at 12° and 750 mm. $N = 8·64$.
$C_9H_9O_2N$ requires $N = 8·59$ per cent.

The mixture of isomeric *propyleneglycol* p-*cyanophenyl ethers* formed a yellow, viscous oil, which crystallised, on long keeping, in almost colourless needles melting between 46° and 67°:

0·2911 gave 20·75 c.c. N_2 (moist) at 21° and 764 mm. $N = 8·16$.
$C_{10}H_{11}O_2N$ requires $N = 7·91$ per cent.

Glycol o-*nitrophenyl ether*, $NO_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, was obtained as a yellow oil, which solidified after keeping for some days. It was crystallised by dissolving in cold ethyl acetate and adding to the solution sufficient light petroleum to produce an opalescence. On introducing a crystal of the substance into the solution cooled in a freezing mixture, a rapid separation of the ether in small, but well-defined, transparent prisms took place. In bulk the crystals had a distinct, although pale, yellow colour; they melted at 35—36°:

0·1732 gave 11·4 c.c. N_2 (moist) at 15° and 766 mm. $N = 7·78$.
$C_8H_9O_4N$ requires $N = 7·65$ per cent.

Glycol m-*nitrophenyl ether*, in the crude state, formed crystals with a very pale yellow tinge. It was recrystallised by dissolving in cold ethyl acetate and adding light petroleum to the solution, when almost colourless, prismatic crystals separated, melting at 87—88°:

0·0929 gave 6·0 c.c. N_2 (moist) at 12·5° and 778 mm. $N = 7·81$.
$C_8H_9O_4N$ requires $N = 7·65$ per cent.

Glycol p-*nitrophenyl ether* was obtained in almost colourless crystals melting at 92—94°, but giving a turbid liquid, which did not become clear until about 100°. In spite of several recrystallisations it was not found possible to obtain a specimen with a sharp melting point. The temperature of fusion of the crystals varied slightly according as benzene, alcohol, or ethyl acetate was employed as the solvent. The sample analysed had been crystallised by dissolving in cold ethyl acetate and adding light petroleum. It formed almost colourless, prismatic needles, softening at 84° and melting at 89—92°:

0·1614 gave 10·4 c.c. N_2 (moist) at 11° and 757 mm. $N = 7·66$.
$C_8H_9O_4N$ requires $N = 7·65$ per cent.

The mixture of *propylene glycol* p-*nitrophenyl ethers* formed a

brown oil, from which one of the isomerides slowly separated in pale yellow, transparent prisms.

These were soluble in hot light petroleum, and on cooling a pale yellow oil separated, which slowly crystallised in large, clear, amber prisms, melting at 65—68°. The crystals were pressed to remove adhering brown oil, and recrystallised from light petroleum, when they melted at 71°:

0·2263 gave 14·15 c.c. N_2 (moist) at 16° and 769 mm. $N = 7·38$.

$C_9H_{11}O_4N$ requires $N = 7·11$ per cent.

The mixture of isomeric *propylene glycol* m-*dimethylaminophenyl ethers* formed a dark-coloured oil, showing signs of incipient crystallisation. An aqueous solution of the *hydrogen oxalates* of the ethers was evaporated under diminished pressure over sulphuric acid, and the residue was crystallised from alcohol. In this way the hydrogen oxalate of one of the isomerides was obtained in white crystals, melting at 133—134°:

0·1913 gave 8·35 c.c. N_2 (moist) at 16° and 764 mm. $N = 5·12$.

$C_{11}H_{17}O_2N,C_2H_2O_4$ requires $N = 4·91$ per cent.

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