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Infrared Spectroscopic Investigations of Hydrogen Bonding in Hindered and Unhindered Phenols¹

BY NORMAN D. COGGESHALL

The hindered phenols which are formed when large alkyl substituents such as *t*-butyl, *s*-butyl or *t*-amyl are added to the two positions *ortho* to the hydroxyl group have markedly different chemical properties compared to the simpler phenols.² The present investigation was made with two objectives: (1) to determine the effect of the large *ortho* substituted alkyl groups on the hydrogen bonding of phenols, and (2) to correlate the chemical and physical properties of the various phenols with their hydrogen bonding behavior.

Infrared absorption spectroscopy offers a very powerful tool for the direct investigation of hydrogen bonding through the study of the radiation absorbing properties of the hydroxyl groups themselves. When a hydroxy compound is in the vapor state or in dilute solution there is little chance for hydrogen bonding complexes to form or to be maintained. Consequently there will be obtained an infrared absorption band at about 2.7 μ which is characteristic of the unperturbed hydroxyl group. However, in solutions of sufficient concentration that hydrogen bonding occurs there is found an absorption band at 3.0 μ characteristic of hydroxyl groups in such complexes. Figure 1 illustrates this phenomenon. In the curves of Fig. 1 and of the other figures in this paper the transmitted energy is plotted *versus* wave length so that absorption maxima are represented by minima in the curves. Here the top curve is for a dilute solution of ethyl alcohol in carbon tetrachloride and there is seen an absorption band at about 2.7 μ . Also seen in this and the other curves is an absorption band at 3.4 μ which is due to carbon-hydrogen valence bond vibrations. This is included in each curve to furnish a visual reference point. In the middle curve is seen the spectrum for an intermediate solution. There is seen to be a weakened band at 2.7 μ and a new band at 3.0 μ . In the lower curve is seen the spectra for a more concentrated solution and here it is seen that 2.7 μ band has completely disappeared, indicating that all the alcohol molecules are involved in complexes. The wave length shift between the absorption of unperturbed hydroxyl groups and bound hydroxyl groups is indicated as $\Delta\lambda$ and may be used as a measure of the strength of the hydrogen bonds formed.^{3,4} A number of substituted phenols have been examined in dilute and concentrated solu-

tions and $\Delta\lambda$ tabulated for each. The consideration of $\Delta\lambda$ in view of the type and position of substituents allows conclusions to be drawn regarding steric hindrance to hydrogen bonding and the chemical properties as dependent upon the substituents.

Experimental Details

The infrared spectrometer was a small sodium chloride prism type. It was supplied with automatic recording equipment which gives records of total energy transmitted as a function of wave length.⁵

In all solutions used the compounds were dissolved in carbon tetrachloride. For solutions of strength of the order of 0.03 mole per liter an absorption cell of 14 mm. length was used. For solutions of about 0.2 mole per liter a cell of 0.91 mm. length was used and for those of about 1 mole per liter a cell of 0.15 mm. length was used. The shorter cells were constructed with amalgamated lead spacers and stainless steel needle valves for filling and sealing.⁶ For the compounds examined in the crystalline state the samples were prepared in the form of thin films. This was done by melting some of the material on a rock salt plate in an oven and pressing another rock salt plate, also oven heated, onto it and allowing them to cool slowly.

The compounds used in this work were supplied by Dr. D. R. Stevens⁷ and Dr. G. H. Stillson² and were believed to be 99% pure with two exceptions which will be discussed later. The carbon tetrachloride was C. P. and was tested in each case for transmission in the hydroxyl region before using. As will be seen from the curves presented the instrument did not have really high resolution in the wave length region. For this reason and also because of a slight uncertainty in exact wave length calibration the absolute wave length values of the unperturbed and shifted hydroxyl bands are not given. In the figures presented the curves are purposely shifted relative to each other in the vertical direction for purposes of clarity.

Data and Discussion

In Fig. 1 is seen the wave length shift $\Delta\lambda$ which occurs for ethyl alcohol in going from a dilute to a concentrated solution. In Fig. 2 may be seen the comparable data for 2,6-dimethyl-4-*t*-butylphenol. Here it is seen that the methyl groups on the *ortho* positions apparently are not

(1) Presented in part before the Division of Physical and Inorganic Chemistry at the Chicago meeting of the American Chemical Society, September, 1946.

(2) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *THIS JOURNAL*, **67**, 303 (1945).

(3) L. Pauling, *ibid.*, **58**, 94 (1936).

(4) J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **162**, 419 (1937).

(5) The optics and recording system for this instrument were supplied by the Perkin-Elmer Corp., Glenbrook, Conn. The instrument itself is not, however, one of their current commercial models.

(6) N. D. Coggeshall, *Rev. Sci. Instruments*, **17**, 343 (1946).

(7) D. R. Stevens, *Ind. Eng. Chem.*, **35**, 655 (1943).

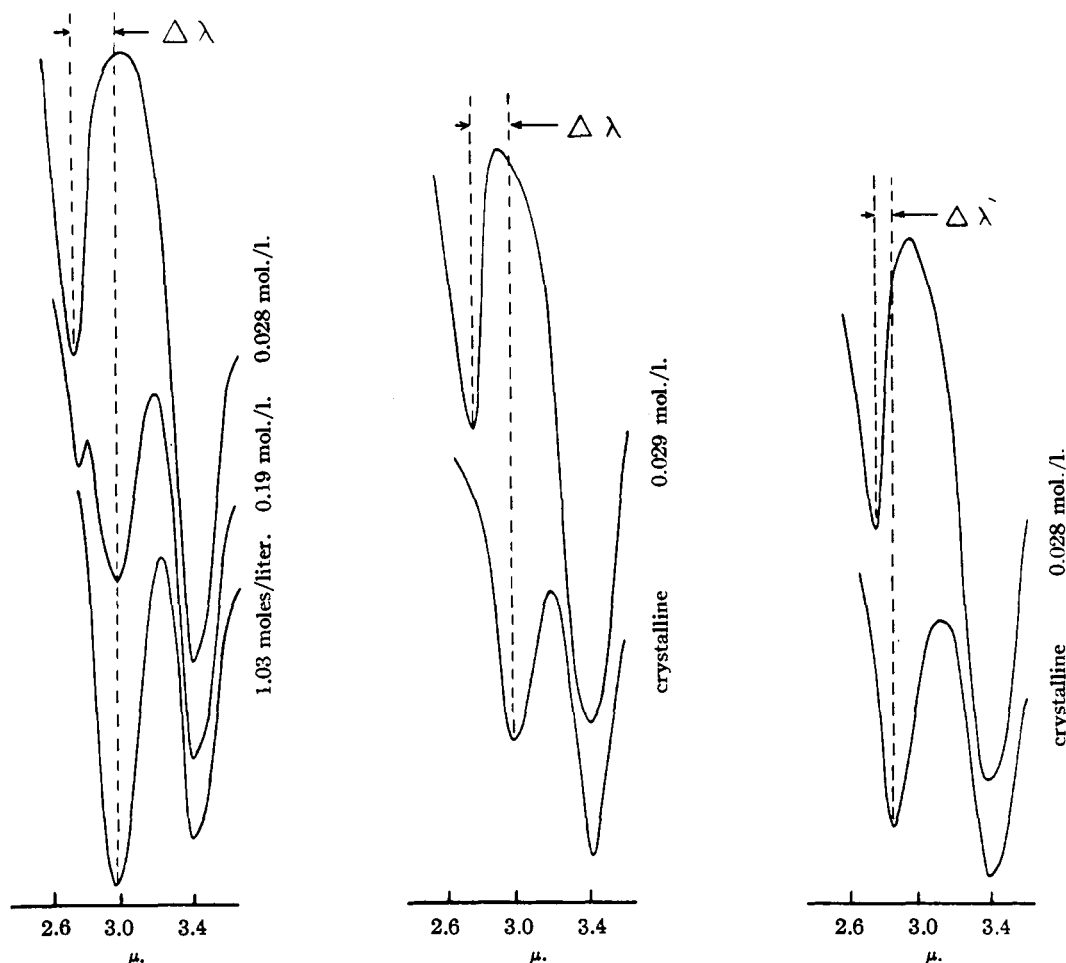


Fig. 1.—Infrared absorption spectra in the hydroxyl region for various concentrations of ethyl alcohol.

Fig. 2.—Infrared absorption spectra in the hydroxyl region for different concentrations of 2,6-dimethyl-4-*t*-butylphenol.

Fig. 3.—Infrared absorption spectra in the hydroxyl region for different concentrations of 2,4-di-*t*-butylphenol.

very effective in hindering molecular association. Other phenols exhibiting wave length shifts comparable to that found for ethyl alcohol are listed in Table I.

Compound	$\Delta\lambda$ in μ
<i>p</i> -Cresol	0.25
<i>p</i> - <i>t</i> -Butylphenol	.45
<i>p</i> - <i>t</i> -Amylphenol	.40
2,6-Dimethyl-4- <i>t</i> -butylphenol	.30

In Fig. 3 may be seen the wave length shift $\Delta\lambda$ which occurs for 2,4-di-*t*-butylphenol in going from a dilute solution to the crystalline state. Here it can be easily seen that the wave length shift is considerably smaller than for the phenol illustrated in Fig. 2. The wave length shift for the present case is 0.12 μ . The large decrease of this shift is believed to be due to weaker hydrogen bonds for this material. The weaker bonds in turn are believed to be due to the hindering effect the

t-butyl group on the *ortho* position has on the approach of the hydroxyl groups to each other when a complex is formed. A case of even smaller wave length shift is seen in Fig. 4 which is for 2-methyl-4,6-di-*t*-butylphenol where $\Delta\lambda = 0.06 \mu$. The decreased shift of this case over the one in Fig. 3 may be ascribed to the increase in hindrance produced by the addition of a methyl group on the other *ortho* position. These two compounds plus others which we have classed in the same group are tabulated in Table II.

Compound	$\Delta\lambda$ in μ
2- <i>t</i> -Amyl-4-methylphenol	0.05
3-Methyl-6- <i>t</i> -butylphenol	.08
2-Methyl-4,6-di- <i>t</i> -butylphenol	.06
2,4-Di- <i>t</i> -butylphenol	.12
2- <i>t</i> -Butyl-4-methylphenol	.12

From Tables I and II can be seen the wave length shifts that occur when both *ortho* positions

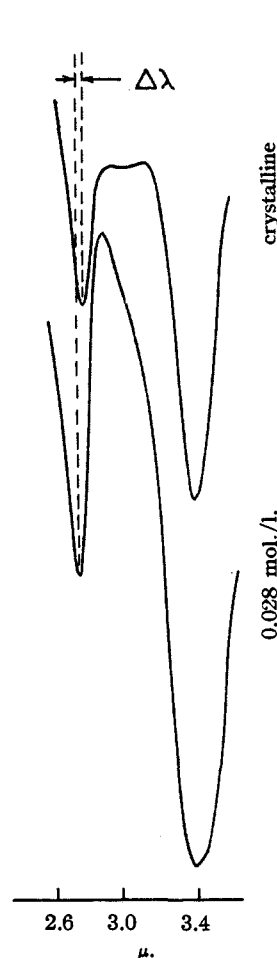


Fig. 4.—Infrared absorption characteristics in the hydroxyl region for unlike concentrations of 2-methyl-4,6-di-*t*-butylphenol.

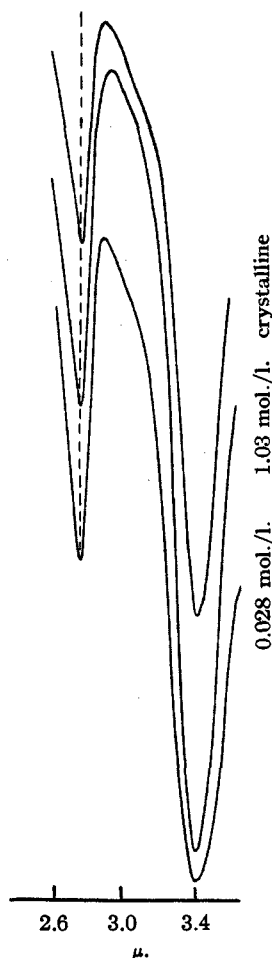


Fig. 5.—Infrared absorption behavior in the hydroxyl region of unlike concentrations of 2,6-di-*t*-butyl-4-methylphenol.

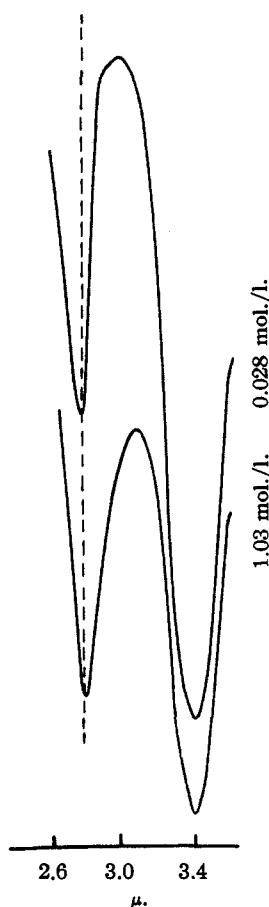


Fig. 6.—Infrared absorption behavior in the hydroxyl region of different concentrations of 2,6-di-*t*-butyl-4-phenylphenol.

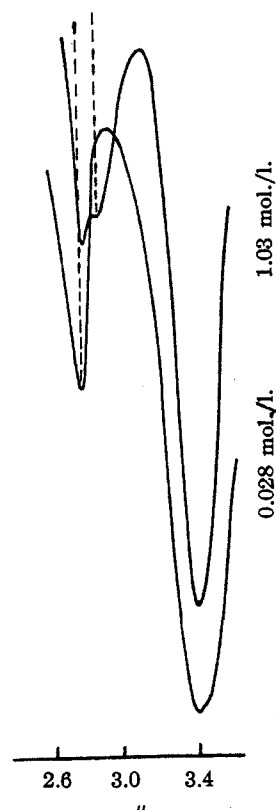


Fig. 7.—Infrared absorption spectra in the hydroxyl region of various concentrations of 2,6-di-*t*-amyl-4-*t*-butylphenol.

are vacant, have only methyl groups on them or have a large group on one such as *t*-butyl. In Fig. 5 may be seen the behavior when large groups are attached to both *ortho* positions. Here are shown the results for a dilute solution, a concentrated solution and a crystalline sample. The reason for testing both the heavy solution and the crystalline sample was to see if the change of phase had any effect on the hydrogen bonding. The indications are that it does not. There was observed for the compound illustrated in Fig. 5 a very small wave length shift which, however, was too small to be demonstrated in the manner used in the other figures. Another example of the behavior of a phenol with both *ortho* positions occupied by large groups may be seen in Fig. 6 which is for 2,6-di-*t*-butyl-4-phenylphenol. The wave length shifts for these compounds and others with similar *ortho* substitutions are given in Table III.

After the data were obtained for the phenols named in the above tables, they were classified ac-

cording to wave length shift, $\Delta\lambda$. For $\Delta\lambda > 0.15 \mu$ the compounds were put in Table I and were termed the unhindered phenols. For $0.04 \mu < \Delta\lambda < 0.15 \mu$ the compounds were put in Table II and were termed the partially hindered phenols. If $\Delta\lambda < 0.04 \mu$ the compounds were put in Table III which represents those compounds termed as hindered phenols. It is very significant that the above classification according to wave length shift also produces a classification characterized by the *ortho* substituents. Those phenols

Compound	$\Delta\lambda$ in μ
2,6-Di- <i>t</i> -butyl-4-methylphenol	0.02
2,6-Di- <i>t</i> -butyl-4-ethylphenol	.02
2,4,6-Tri- <i>t</i> -butylphenol	.01
2,4-Di- <i>t</i> -butyl-4-diisobutylphenol	.02
2,6-Di- <i>t</i> -butyl-4-phenylphenol	.03
2,6-Di- <i>s</i> -butyl-4-methylphenol	.01

in Table I have no substituents on the *ortho* positions larger than methyl groups. The phenols in Table II have one *ortho* position occupied by a large group and the other position either vacant or occupied by a small group. The phenols in Table III have both *ortho* positions occupied by large groups. From these results we may definitely conclude that hydrogen bonding in phenols is sterically hindered by large groups on the *ortho* positions. This is important when a model of the hydrogen bond is considered and this will be discussed further below.

The compounds listed in Table III are seen to be of the same class as those designated by Stillson, Sawyer and Hunt as hindered phenols because of their chemical properties.² The hindered phenols have certain chemical properties quite in contrast to the simple phenols and they are listed below³ (a) insoluble in water, aqueous alkali of any strength and sparingly soluble in alcoholic alkali similar to Claisen's solution. (b) Failure to give the customary phenol coloration with aqueous or alcoholic ferric chloride solution. (c) Will not react with metallic sodium in anhydrous petroleum ether or diethyl ether solutions, even at reflux temperatures. (d) Will not form derivatives such as acetates or benzoates by the methods usually applicable to phenols in preparing such derivatives.

In designating these phenols as hindered phenols the above mentioned investigators assumed that the addition of the large groups on the *ortho* positions might interfere with the normal functions of the hydroxyl group by steric hindrance and thus be responsible for their peculiar chemical properties. The present work confirms this assumption insofar as it shows in a direct manner that the large *ortho* substituents are responsible for steric hindrance to hydrogen bonding. The fact that in the hindered phenols with their particular chemical properties the functions of the hydroxyl group are masked or hindered by the large *ortho* substituents emphasizes strongly the importance of the hydroxyl groups for the contrasting chemical behavior of the simpler phenols.

The phenols included in Table II and classified here as partially hindered fall into the so-called cryptophenol class.^{2,9} These phenols are insoluble in water and sparingly soluble in aqueous alkali although soluble in alcoholic alkali solutions of the Claisen solution type. Their solubility characteristics are intermediate between those of the simple phenols and those of the hindered phenols. This is additional evidence that the degree of masking or inactivation of the hydroxyl group by steric hindrance is instrumental in controlling the solubility characteristics.

Since the hydrogen bond represents an attractive force which must be overcome when the substance is to be vaporized it is to be expected that

(8) The author is indebted to Dr. G. H. Stillson of this Company for preparing this listing of properties.

(9) J. B. Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938).

in a series of *ortho*, *meta* and *para* isomers, the one with the weakest hydrogen bond would in general have the lowest boiling point. The infrared absorption data presented here indicate that the one with the weakest hydrogen bond would be the *ortho* isomer and this is in general agreement with actual experimental boiling point determinations. These latter show that the addition of a *t*-butyl or other large alkyl group to the *ortho* position in a phenol produces a smaller increase in boiling point than when added to a *meta* or *para* position.¹⁰

A scrutiny of Tables I, II and III indicates that the type and order of substitution on the 3, 4 and 5 positions have at best only a small second order effect on the hydrogen bonding characteristics.

In their studies of hydrogen bonding in various hydroxy compounds in which they obtained quantitative data for different solutions Fox and Martin⁴ considered three possible types of hydrogen bond complexes: (a) A dimer type of complex in which the hydrogen atom of one of the hydroxyl groups is held between the two oxygen atoms while the other hydrogen atom is "free." This corresponds to the absorption characteristics of one hydroxyl group being changed and one being unchanged. (b) A polymerized type of complex wherein the hydroxy compounds are held in a long chain by hydrogen bonding forces. In this model the hydrogen atom of the hydroxyl group of any one of the molecules is held between the oxygen atom of that molecule and the oxygen atom of the successive molecule in the chain. This model corresponds to all except the terminal hydroxyl groups being perturbed. (c) A dimer type of complex wherein both hydroxyl groups are involved. They compared the theoretical and experimental results assuming the different types of complexes and concluded that type (c) is correct. This type (c) complex corresponds to the hydrogen bond forces being due to van der Waals dipole-dipole interactions. Since for such an interaction the potential energy varies inversely with the sixth power of the distance of separation,¹¹ any change in the separation distance will greatly affect the strength of the bond. The present results may be interpreted as consistent with this model as the groups in the *ortho* positions increase the minimum distance of separation and greatly reduced hydrogen bonds result as evidenced by the very small wave length shifts.

From Tables I, II and III it is seen that for all phenols examined there is agreement between the classification according to wave length shift and classification according to substitution on the *ortho* positions. Although exceptions may be found the results in the tables seem conclusive enough to formulate tentative general rules for the study of phenols of unknown structure. Thus if a phenol exhibits a wave length shift which fits any one of the three classifications, reliable conclu-

(10) Robert S. Bowman, Mellon Institute, Pittsburgh, Pa., unpublished material.

(11) H. Margenau, *Rev. Modern Phys.*, **11**, 1 (1939).

sions concerning its *ortho* substitutions may be possible.

It was mentioned earlier that two compounds examined were not of the 99% purity believed true of the others. These two compounds were 2,6-di-*t*-amyl-4-*t*-butylphenol and 2,6-di-*t*-amyl-4-methylphenol. Those compounds (liquid at room temperature) were somewhat discolored and were not believed to be of high purity from their history. Their infrared spectra gave interesting results in suggesting the presence of mono-substituted phenols as impurities. Figure 7 shows the results for 2,6-*t*-amyl-4-*t*-butylphenol. As can be seen there is an extra absorption band which shows up for the heavy concentration. This band is indicated by the dashed line to the right and is so close to the main OH absorption band that the two are not resolved. This second band is believed to be due to mono-substituted phenols, *i. e.*, molecules with only one large alkyl group on an *ortho* position. This explanation is confirmed by the fact that no such band appears in the spectrum of the dilute solution. A similar doublet was observed for 2,6-di-*t*-amyl-4-methylphenol and its cause also is believed to be the same. The behavior of the spectra of the concentrated solutions for these cases suggests a method for checking the purity of phenol samples. To test this a number of synthetic mixtures were prepared from mono and di-substituted phenols of high purity. The spectra of these mixtures confirmed the feasibility of checking the purity in this manner.

Acknowledgment.—The author is indebted to Dr. D. R. Stevens and Dr. G. H. Stillson for kindly supplying the compounds studied, also to Dr. M. Muskat for supporting this work and

to Dr. P. D. Foote, Executive Vice-President of Gulf Research and Development Company, for permission to publish this material.

Summary

An infrared absorption spectroscopic investigation has been made of the hydrogen bonding in various phenols. The wave length shift of the hydroxyl absorption band attendant to the formation of the hydrogen bond was measured for each phenol. The results allow a classification of the phenols according to the magnitude of this shift. For the wave length shift $\Delta\lambda > 0.15 \mu$ the compounds are classed as unhindered phenols, for $0.04 \mu < \Delta\lambda < 0.15 \mu$ they are classed as partially hindered phenols, and for $\Delta\lambda < 0.04 \mu$ they are classed as hindered phenols. The unhindered phenols were those with either no or small substituent groups on the *ortho* positions; the partially hindered phenols were those with either one *ortho* position vacant and the other having a large alkyl group, or one small *ortho* substituent and one large one; the hindered phenols were those with large alkyl groups on both *ortho* positions. These results directly indicate that the *ortho* groups offer steric hindrance to hydrogen bonding. This confirms postulated reasons for the peculiar chemical behavior of the hindered phenols. Evidence is obtained that the substituents on the 3, 4 and 5 positions are not important in affecting hydrogen bonding. A method is provided for aid in determining position of substitution in phenols of unknown structure. A method is indicated for the study of purity of di-substituted phenols.

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Physical Properties Supporting the Phenolic Nature of a Certain Hindered Phenol; A Synthesis of *t*-Butyl *p*-Tolyl Ether

BY JOSEPH B. MCKINLEY

Stillson and co-workers^{1a,b} have described a class of compounds called the hindered phenols. These are phenols carrying large branched groups, in the positions *ortho* to the hydroxyl, which interfere with its activity to such an extent that the phenols, upon casual examination, might easily be considered to have an ether structure. The above workers, however, presented chemical evidence as to the true phenolic nature of their compounds. This paper presents physical data which substantiate the presence of a hydroxyl group in one of their products; it will be called compound A and is considered to be 2,6-di-*t*-butyl-4-methylphenol (I). This hindered phenol was selected for the examination because it has been

contended² that, using substantially the same conditions of preparation as described by Stillson and co-workers and also by others,^{3a,b} *t*-butyl 2-*t*-butyl-4-methylphenyl ether (II) is actually formed.

The most direct proof that compound A is not (II) would be to synthesize (II).¹ Repeated attempts to accomplish this by several syntheses were unsuccessful, but the preparation of the homologous *t*-butyl *p*-tolyl ether (III) was accomplished. Although it was not the compound originally desired, it is a *t*-butyl aryl ether such as (II) and its physical properties are used below to help confirm the phenolic structure of compound A.

(2) McNab, Wilson and Winning, U. S. Patent 2335,017 (Nov. 23, 1943).

(3) (a) Stevens, *Ind. Eng. Chem.*, **35**, 655 (1943); (b) Stevens and Gruse, U. S. Patent 2,365,592 (Dec. 9, 1941).

(1) (a) Stillson, Sawyer and Hunt, *Text JOURNAL*, **67**, 308 (1945); (b) Stillson, *ibid.*, **68**, 732 (1946).