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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[CONTRIBUTION FROM MELLON INSTITUTE AND GULF RESEARCH & DEVELOPMENT COMPANY]

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 contended[2] 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). 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.

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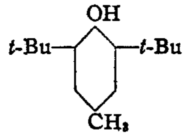
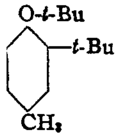
(1) (a) Stillson, Sawyer and Hunt. THIS JOURNAL, 67, 303 (1945); (b) Stillson, *ibid.*, 68, 722 (1946).

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

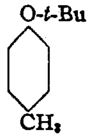
(3) (a) Stevens, *Ind. Eng. Chem.*, 35, 655 (1943); (b) Stevens and Gruse, U. S. Patent 2,265,582 (Dec. 9, 1941).



(I)



(II)



(III)

The actual synthesis of (III) involved treating *p*-cresoxymagnesium bromide with *t*-butyl chloride, using ether as the medium. In preliminary experiments, special precautions were taken to exclude water and water vapor from the reaction system. When using 1.33 moles of *p*-cresoxymagnesium bromide per mole of *t*-butyl chloride and a set reaction procedure (see details below) yields of the ether of the order of 3 to 7%, based on the *t*-butyl choride, resulted. Upon duplicating the work, with the exception that water was deliberately added to the reaction mixture, better results were obtained,[4] as is shown by Table I.

TABLE I

Moles water added/mole of *p*-cresoxymagnesium bromide	% Yield of *t*-butyl *p*-tolyl ether
0.00	3.0–7.0
.15	9.2
.30	20.9
.45	17.9

Figure 1 shows the infrared absorption spectra curves in the 2.6 to 3.4 μ region of carbon tetrachloride solutions of compound A, the ether (III), ethyl alcohol, and 2,4 di-*t*-butylphenol.[5] These curves represent energy transmitted through the samples plotted against wave length so that absorption maxima are represented by minima in the curves. They are displaced with respect to one another along the vertical axis to make comparison convenient. The solutions contained 0.03 mole of compound per liter of solvent. The spectra given are substantially those of the dissolved compounds, for the solvent shows negligible absorption in the spectral region shown.

The spectrum of the solution of ethyl alcohol shows absorption bands at about 2.7 and 3.4μ. The former is known to be caused by the hydroxyl group and is attributed to the stretching vibrations of the valence bond joining the hydrogen and oxygen. The latter band is caused by the stretching vibrations of the carbon–hydrogen bonds in the alcohol. These bands are found in spectra of all compounds containing hydrogen–oxygen and carbon–hydrogen bonds.[6] They are exhibited, for example, in the spectrum of the solution of 2,4 di-*t*-butylphenol, a compound of accepted phenolic structure.

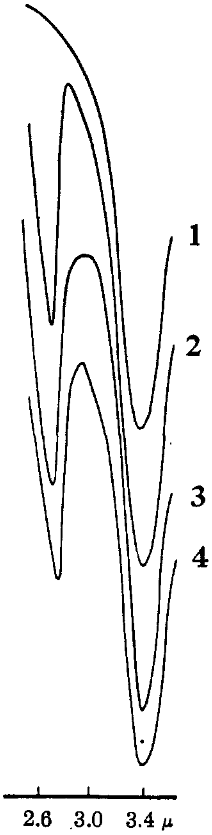


Fig. 1.—Infrared spectra of dilute carbon tetrachloride solutions of *t*-butyl *p*-tolyl ether, curve (1); compound A, curve (2); ethyl alcohol, curve (3); and 2,4-di-*t*-butylphenol, curve (4).

The spectrum of the solution of compound A is substantially identical to the spectra of the solutions of ethyl alcohol and 2,4-di-*t*-butylphenol. It thus seems safe to conclude that compound A contains a hydroxyl group and is a phenol. Certainly it is not an ether, for the spectrum of the solution of the ether (III) does not show an absorption band at 2.7μ.

Further confirmation that compound A is a phenol may be had by referring to its physical properties and those of 2-*t*-butyl-4-methylphenol and the ether (III), given in Table II. If compound A actually had structure (II), it would be expected to have a lower density and refractive index than (III). This is because its aryl group would be much more highly alkylated (*i.e.*, it would carry a much greater percentage of its carbon atoms in alkyl groups) than that of (III) and a study of compounds containing aryl groups from this standpoint indicates, in general, that the more highly alkylated the aryl group in otherwise corresponding compounds, the lower will be the density and refractive index. Actually the data show that the density and refractive index values for compound A are higher than these values for (III), indicating that it is not the ether. On the other hand, the observed relationship seems quite reasonable if compound A is a phenol, since phenols have higher densities and refractive indices than do the corresponding ethers. Compare, for example, the properties of 2-*t*-butyl-4-methylphenol and those of (III).

TABLE II

Substance	d^{75}_4	n^{75}_D[a]
2-*t*-Butyl-4-methylphenol	0.9247	1.4969
t-Butyl *p*-tolyl ether (III)	.8688	1.4626
Compound A	.8937	1.4859

[a] Determined with a Pulfrich refractometer enclosed in an air oven at 75°. The modified instrument gave a n^{75}_D of 1.32436 for water.

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(4) The reason for the advantage gained is not known. The effect was discovered in exploratory runs which showed that good yields could be obtained when aged (partially hydrolyzed) *p*-cresoxymagnesium bromide was used for the reaction instead of fresh product.

(5) The data were obtained and interpreted by Dr. N. D. Coggeshall. He has described the experimental method and has obtained infrared spectra of several hindered phenols other than compound A (THIS JOURNAL, 69, 1620 (1947)). These spectra when examined in light of the discussion which follows in the text obviously show that the compounds studied have phenolic structure.

(6) In more concentrated solutions than those employed, many compounds containing a hydroxyl group associate by hydrogen bonding. The bonding involves hydroxyl groups and in spectra these bonded hydroxyls are typified by an absorption band at about 3.0μ. Bonding is negligible in solutions as dilute as those employed.

Experimental

Phenolic Materials.—2,4-Di-*t*-butylphenol (b. p. 146.0° at 20 mm.; m. p. 56.5°), 2-*t*-butyl-4-methylphenol (b. p. 126.0° at 20 mm.; m. p. 52.3°), and compound A (b. p. 147.0° at 20 mm.; m. p. 70.0°) were obtained from G. H. Stillson and co-workers[1a] and D. R. Stevens.[3a] The materials when received were recrystallized from petroleum ether and refractionated through a 20-plate column at 20 mm. Products distilling at a constant temperature (±0.05°) and having freezing point curves indicating negligible impurities were prepared. These were used for determination of the properties given in the text.

***t*-Butyl *p*-Tolyl Ether.**—Typically, in the set reaction procedure adopted wherein water was not added to the reaction mixture, recrystallized and refractionated Eastman Kodak Company *p*-cresol (2.42 moles) in 484 ml. of absolute ether was added dropwise with stirring over a period of two hours to 1033 g. of Grignard reagent solution, which was found by titration[7] with acid to contain 2.42 moles of ethylmagnesium bromide. The single-phase stirred reaction mixture resulting was seeded with previously prepared product, causing the *p*-cresoxymagnesium bromide to precipitate gradually.[8] The slurry was filtered rapidly, taking care not to separate all the ether from the bromide, thus protecting it from other than minor hydrolysis due to water vapor in the air. It was then washed three times with absolute ether, using the same precaution. The ether-wetted bromide (estimated to be 2.20 moles, considering transfer losses) was added to 1.65 moles of dry *t*-butyl chloride dissolved in 1100 ml. of absolute ether.[9] The slurry was refluxed and stirred for thirteen hours, during which time it became so thick as to make stirring useless. It then stood forty hours at room temperature. The reaction mixture was shaken with one liter of water to obtain an ether layer and an aqueous slurry. The ether layer was decanted and washed with 10% alkali several times to remove completely the *p*-cresol,[10] which is a main reaction product. It was then washed with water and dried with anhydrous sodium carbonate. The aqueous slurry, associated with a small amount of undecanted ether layer, was treated with sufficient concentrated hydrochloric acid to dissolve the solids, and the clear solution was extracted with ether. This second ether layer was washed and dried as was the first, and the two were combined. The solvent was distilled off at atmospheric pressure until the still-pot temperature reached 100°. Last traces were removed by reducing the pressure to 20 mm. and bubbling nitrogen through the product at room temperature. The residue distilled almost entirely at 82.5° at 10 mm. It had substantially the same properties as the specially purified *t*-butyl *p*-tolyl ether described below; yield was 0.115 mole (7.0%).

From several similar preparations, 100 ml. of product was composited and fractionated through a 20-plate column. Ether having a constant boiling point of 82.5° at 10 mm. was collected and found to have the properties given in Table II. In addition, it had a d^{20}_4 of 0.9138 and a n^{20}_D of 1.4879. Time–temperature freezing point curves showed that it froze at −37.7 ± 0.1° or −32.2 ± 0.1°. The freezing point of −37.7° resulted when seeding was done with freshly crystallized ether. The freezing point (obviously of the stable crystalline form) of −32.2° was obtained when seeding was done with crystalline ether which had stood at −40.0 to −80.0° for three or four days.

The ether rearranged to 2-*t*-butyl-4-methylphenol (identified by mixed melting point) when treated with from 1 to 5 per cent. of concentrated sulfuric acid for three hours at 90°. Refluxing alone at atmospheric pressure caused it to rearrange very slowly. This was noted by applying a sensitive spot test for phenols.[11] Unrefluxed material gave a negative test, but when it had been refluxed for twenty-six hours a slight positive test was obtained.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82; mol. wt., 164.2. Found: C, 80.69; H, 10.13; mol. wt., 169.0.

Acknowledgment.—The criticisms of Dr. W. A. Gruse and Dr. D. R. Stevens during the preparation of this manuscript were gratefully accepted.

Summary

Further evidence is given to show that the compound considered by previous investigators[1,3] to be 2,6-di-*t*-butyl-4-methylphenol is truly a phenol. Confirmation resulted from a comparison of densities, refractive indices, and infrared spectra of this and related compounds.

The synthesis of *t*-butyl *p*-tolyl ether, a new compound, is described.

PITTSBURGH, PENNA. RECEIVED DECEMBER 28, 1946

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(7) Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

(8) The time and speed of the formation of the *p*-cresoxymagnesium bromide are unpredictable. Often it forms suddenly when 75 to 100% of the theoretical amount of *p*-cresol has been added. The bromide formation is exothermic; thus, when it forms suddenly violent boiling of the reaction mixture results.

(9) Water was added at this point in the runs using it.

(10) Apparently formed by the reaction $p\text{-}CH_3C_6H_4OMgBr + t\text{-}C_4H_9Cl \rightarrow p\text{-}CH_3C_6H_4OH + i\text{-}C_4H_8 + MgBrCl$.

(11) Platkonskaya, *J. Applied Chem.* (*U. S. S. R.*), **10**, 202 (1937); *C. A.*, **31**, 4232 (1937).