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A SURVEY OF THE LITERATURE CONCERNING HINDERED PHENOLS
AND A PRELIMINARY STUDY OF THE OXIDATION OF THE HINDERED
PHENOL, 2, 6-DI-TERT-BUTYL-4-METHYLPHENOL

By

John M. Erickson

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I. INTRODUCTION

Antioxidants play a very important part in many chemical industries in protecting petroleum products, rubber, foodstuffs, resins, fats, oils, soaps, and a variety of chemicals from atmospheric oxidation during their manufacture, storage, and use. Phenolic compounds comprise one of the important groups of antioxidants and within this group are the hindered phenols, many of which are very efficient oxidation inhibitors. Hindered phenols are monohydric phenols whose two ortho-positions are occupied by tertiary butyl or larger groups thus hindering the phenolic properties of the compound. They are insoluble (132) in aqueous or alcoholic alkali solutions and will not respond to most of the conventional tests and reactions of phenols.

This study was concerned with this class of compounds and especially with 2,6-di-tert-butyl-4-methylphenol or 2,6-di-tert-butyl-p-cresol (hereafter designated DBPC) and its use as an antioxidant in petroleum oils. It was hoped that by investigating the mechanism of the oxidation, a further insight into the effect of the substituent groups would be attained with the aim that such information might lead to the synthesis of still more effective antioxidants.

Section II is a review of the literature covering general information on hindered phenols, their preparation, detection, separation, purification, properties, and uses. Many references which explain or offer theories of oxidation reactions are listed.

Though they do not always pertain directly to hindered phenol, they may point the way towards a possible explanation of the mechanism of the oxidation of these hindered phenols. The literature covering the development of reactions and reaction conditions which lead to the formation of trialkylated phenols has been reviewed to 1937 by Dreyer, et al. (36).

The details of the investigation of the oxidation of DBPC and the findings are given in Section III. Considerable auxiliary work was done in connection with this study but was not included here if it did not deal directly with the final procedures used.

Section IV is a discussion of the experimental data collected and the limitations of the work. A brief summary of the entire investigation is found in Section V.

Some suggestions and recommendations for further study are presented in Section VI and perhaps the most valuable contribution of this work is the aid it can give to continued work on this study.

II. REVIEW OF THE LITERATURE

A. General

An extensive literature survey was undertaken to collect information on hindered phenols in general and on DBPC in particular. It was oftentimes difficult to decide just what to include and what not to include. The underlying philosophy has been to include all literature concerned with DBPC and its use as an antioxidant in petroleum oils and also such literature as might give information on very closely related phenols or might suggest ideas for the separation, purification and identification of phenols and their oxidation products, for the mechanism of the oxidation of the hindered phenols, and for further research. The information on patents and from foreign language books and periodicals was obtained for the most part from Chemical Abstracts.

Zuidema (157) called the investigations of Moureu and Dufraisse (87) in 1926 the "pioneer work" on antioxidants. Since then a tremendous amount of effort has been put forth to try to understand the effectiveness of certain types of compounds and to find new and better oxidation inhibitors.

Occasionally the stability of certain natural petroleum products were noted even though the reasons for their stability was a mystery. For example, Razumov (95) noted that cracked gasolines from Ekhabl crude oil exhibited exceptional stability. It was later found to contain natural inhibitors responsible for this marked

stability. Monohydric phenols, in which ortho- and para-cresols and 1,3,5-, 1,2,4-, and 1,4,2-xlenols were identified, were found among these natural inhibitors. Larsen and co-workers (66) came to a like conclusion after studying the oxidation characteristics of pure hydrocarbons. They found that polynuclear aromatics were most stable probably due to formation of inhibitors on oxidation and decided that the stability of a lubricating oil was not due to the basic hydrocarbon but to the natural inhibitors it contained. (This article gave some of the details of the analytical work involved in the study, i.e., methods of determining acidity, saponifiable material, carbonyl values, alcohols, peroxides, etc.).

The lack of reactivity of hindered phenols led many investigators to believe that these compounds were phenolic ethers rather than free phenols. Stillson, Sawyer, and Hunt (139) described the preparation of some of these substances and presented evidence to indicate the presence of the hydroxyl group in one of them, namely, DBPC. However, McNab, Wilson, and Winning (74) claimed that substantially the same set of conditions gave tert-butyl-2-tert-butyl-4-methylphenyl ether. McKinley (73) on the other hand, upheld Stillson's results by being unsuccessful in attempting to synthesize the ether and then by a comparison of densities, refractive indices, and infrared spectra was able to prove that the compound was truly a phenol and not an ether. Kunc, et al., (64) gave additional physical evidence that this substance was a phenol. The lack of reactivity of the hydroxyl group is due to the steric hinderance while the lack

of ring activity may also be due in part to the insolubility of the substance and to the fact that the three active positions of the benzene ring are substituted.

After Stillson, et al., (139) showed these polyalkylphenols to be strongly hindered and to undergo the usual phenol reactions only sluggishly, if at all, Whitaker (153) undertook to determine if this decreased activity would be manifest in the catalytic hydrogenation of these compounds and found that it was.

Some interesting work has been done involving the ultraviolet absorption spectra of phenols. Stendstrom and co-workers (107,108) as early as 1925 demonstrated that the shift of the phenol spectra induced by the addition of sodium hydroxide was due to the formation of the phenolate ion and from their data determined a dissociation constant for phenol. Lemon (67) reported the ultraviolet spectra of 22 phenolic compounds and noted that in every case the addition of alkali caused a shift of the absorption band towards the visible. Coggeshall (25) was able to classify phenols as hindered (both ortho-positions occupied by large groups, such as, the tert-butyl group), partially hindered (one ortho-position occupied by a large group, the other by a small group or unsubstituted), and unhindered (the ortho-positions either unsubstituted or occupied by small groups) as a result of the shift of the hydroxyl absorption band attendant on the formation of the hydrogen-bond in solution. Ortho-groups offer steric hinderance to hydrogen bonding. This confirms the postulated chemical behavior of hindered phenols. The same type

of hinderance which influences hydrogen bonding is effective in hindering intermolecular association effects which influence the ultraviolet absorption spectra of the phenols. The hindered phenols show very little spectral change between examination in paraffin and in polar solvents such as ethyl alcohol while large changes are found in the case of partially hindered and unhindered phenols.

The differences have been interpreted as due to the different degrees of proximity possible between the hydroxyl group of the phenol and the polar groups of the solvent. In view of these facts Coggeshall and Glessner (26) made a study of the ultraviolet spectra of substituted phenols in alcoholic solutions containing sodium hydroxide. They first verified previous work that the spectral shift was due to the formation of the phenolate ion. They then found that unhindered phenols gave evidence of complete ionization in 0.1 molar sodium hydroxide. Partially hindered phenols were only partially ionized at this concentration but completely ionized at 0.5 molar sodium hydroxide. The hindered phenols were not completely ionized even in 5.0 molar solution. This led to the conclusion that the process of ionization was the result of direct collision or of a small distance of approach between the phenolic hydroxyl group and other molecules or ions. Therefore, shielding of the hydroxyl group such as that offered by large groups in the ortho-positions was effective in reducing the ionization. Thus, a method for determining the acidity of various phenols was developed and important information pertinent to the consideration of the ionization process provided.

Murray (89) made use of the ultraviolet spectra to determine the total phenol content of gasolines with an ultraviolet spectrophotometer by working with the 290 millimicron band and an empirical extinction coefficient of 24.

A number of references are of interest at this point which tend to show the development of the use of phenolic compounds, especially the hindered phenols, as oxidation inhibitors in oils and petroleum products. Haslam and Frölich (50) in 1927 in one of the earlier articles on the oxidation of mineral oils discusses the mechanism of the reaction and the use of negative catalysts without mentioning the hindered phenol type. However, their conclusions may very well apply to this type. They stated that the antioxidant added may be: (1) oxidized and thus lose its protective power, (2) evaporated directly without being subject to oxidation, (3) subject to both (1) and (2), or (4) lessened in activity as a result of reactions caused by heat, i.e., intramolecular condensation or polymerization in the catalyst itself or between the oil and the catalyst. Also a possibility is the fact that a positive catalyst may be formed in the system. Morris and Riemenschneider (86) show the wide variety of types of substances that exist in the study of the antioxidant properties of a number of phenolic and other compounds. They list the order of activity of different types of compounds. In 1941, Fenske, et al., (41) discussed the oxidation of lubricating oils and the factors influencing the oxidation with no more than just mentioning antioxidants. However, about the same time, Olcott (92)

reported that any acidic inhibitor will promote the action of any phenolic inhibitor and that combinations of the two are often advantageous. A patent to Stevens and Gruse in 1940 (117) was one of the first to relate to the use of 2,4,6-trialkylated phenols where at least one of the ortho-substituents contain three or more carbon atoms to inhibit oxidational deterioration of materials such as motor fuels. Kluge and Knowles (59) describe the preparation of 2,6-di-tert-butyl-4-chlorophenol which when present in an A.S.T.M. turbine oil oxidation test required 1120 hours to reach a neutralization number of two compared to 75 hours for the untreated oil. Kroger (63) studied a large number of antioxidants including aromatic hydroxy compounds in lubricating oil and tried to draw some conclusions of effectiveness versus molecular makeup and structure. He found no correlation between the effectiveness of a compound and its molecular size, boiling point, molecular refraction, dielectric constant, dipole moment, or parachor. A study was made by Rosenwald, Hoatson, and Chenicek (99) in 1950 of a number of methyl- and butyl-substituted phenols as gasoline stabilizers and the effects on stabilizing potency of the number of substituents and their size, configuration, and position. The potency of the phenol as a stabilizer increased with increased number of substituents but the size of the substituent had little effect. Ortho-substitution was most effective and the tertiary butyl group gave the best results. According to their study 2,4-di-methyl-6-tert-butylphenol was the best stabilizer tested. Their paper gave physical properties and methods of preparation with literature references for

about 35 substituted phenols. Kitchen, Albert, and Smith (58) investigated a number of di- and trialkyl-substituted phenols as antioxidants for synthetic rubber. They concluded that the 2,4-dialkylphenols and the 2,4,6-trialkylphenols which have the methyl group in the para-position are more effective than similar and isomeric compounds with larger para or meta substituents.

These investigations have shown that the class of compounds known as hindered phenols are truly phenols and not ethers, that they are effective and important antioxidants, and that perhaps, with increased knowledge of the effect of substituents, better antioxidants can be produced.

B. Preparation of Hindered Phenols

The preparation of hindered phenols has been studied by a number of investigators and several different methods have been developed for their production. Many of these methods have evolved from schemes originally devised to produce mono- and dialkylated phenols. Ipatieff, Pines, and Friedman (53) reported the preparation of some alkylated phenols in 1938 by reacting phenol with isobutene and diisobutene with and without scission of the C-C linkage. A Friedel-Crafts type of reaction was reported by Olin (93) for the alkylation of phenol, dihydroxy phenols such as resorcinol, cresol, naphthol, etc.. Catalysts such as aluminum chloride, iron, aluminum, or zinc were and were not used. Details were given for the reaction of secondary and tertiary alkyl halides with phenol in the presence of iron rust. Mavity (81) describes

the alkylation of phenolic compounds by a modified Friedel-Crafts' catalyst. The method of preparing the catalyst and details for the preparation of amylphenol were given.

Various alcohols have been used with phenols to form alkylated products. The information on this method of producing substituted phenols was meager but it is highly probable that only the mono-derivatives were produced. Beamer (9) prepared a tert-butylphenol by reacting tert-butyl alcohol with phenol in the presence of concentrated sulfuric acid and below 15° C. Dow Chemical Company (34) reported a similar reaction and removed the water as rapidly as it was formed by vaporization. Suitable stable dehydration and condensation catalysts were listed and included the acid-activated bleaching earths "Retrol" and "Tonsil", concentrated sulfuric acid, ferric chloride, zinc chloride, and sulfonic acids. Another reaction of this type was described by Read (96).

The early study of the preparation of certain dialkyl phenols was due as much to their use as germicides and antiseptics as to their use as antioxidants. A patent was issued to Moyle and Van Duzee in 1940 (88) for a method of making dialkylphenols such as 2,ethyl-5-sec-amylphenol and 2-tert-butyl-5-propylphenol for use as germicidal compounds. Carpenter (19) described the preparation of substituted phenols, such as 2-methyl-3-isopropylphenol, which were used as antiseptics and antioxidants for soaps.

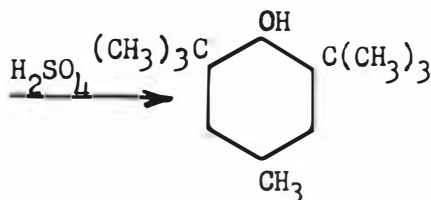
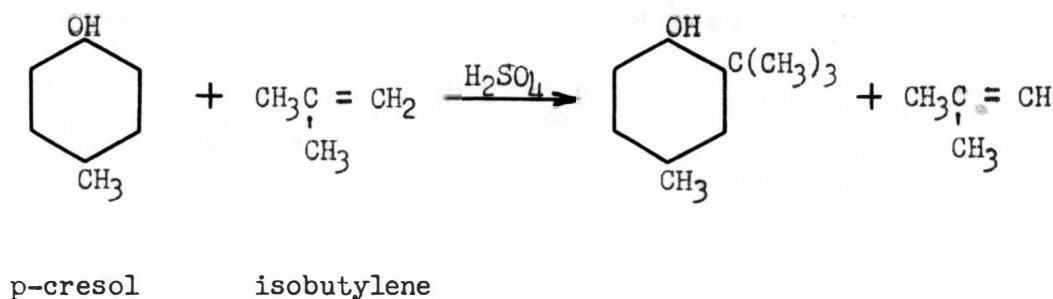
As was mentioned above, various methods have been reported for introducing alkyl groups on to the nucleus of phenol. The hindered

phenol, 2-6-di-tert-butylphenol, was produced by Stillson and Sawyer (138) by the treatment of a p-halophenol with isobutylene in the presence of a catalyst and the removal of the halogen from the reaction product with an alkali metal in anhydrous ammonia. They mentioned the use of the product as an antioxidant in lubricating oils. Stevens and McKinley (124) produced dialkylphenols by alkylating a mixture of meta- and para-cresols with a tertiary olefin such as isobutylene. The preparation of 3-methyl-4-tert-butylphenol, used as an antioxidant for petroleum products and in the synthesis of thymol, was accomplished by Stevens and Bowman (114) from meta-cresol and isobutylene.

Some of the early antioxidant mixtures were produced and used effectively without knowing exactly what the specific compounds were which were responsible for the inhibition of oxidation. Stevens and Gruse (115) in 1937 prepared a mixture which served as an antioxidant by treating a cracked petroleum distillate with a mixture of a phenol such as cresylic acid and sulfuric acid and separating the product. They did not report the identity of this product and it is presumed it was not known. These two investigators (116) in 1940 cited the preparation of a reaction product of a phenol and the hydrocarbon constituents normally found in cracked gasolines which inhibited the oxidation and gum formation in gasolines on exposure to air and light. Dryer (35) produced an addition product for gasolines by effecting the reaction of a phenol such as a lignite-tar fraction with an olefin such as isobutylene

in the presence of sulfuric acid containing a small amount of boric acid at 120° F. In these three instances, the nature of the final product could hardly be stipulated exactly since the reaction mixture was probably quite complex. However, it is plausible to assume that alkylated phenols were formed and were the oxidation inhibitors.

Turning now to the development of methods which produced the trialkylated phenols, the one which involved the use of sulfuric acid as the catalyst and an alkylating agent such as isobutylene seems to have received the most widespread attention. The mono-alkylphenols were first produced (46) but work was soon progressing on the production of trialkyl derivatives. Some of the various modifications of this scheme follow. The basic reaction is of the type:



2,6-di-tert-butyl-p-cresol

Stevens and Gruse (121) in 1941 received a patent for this same reaction. Later, Stevens, with Nickels (129) and again, with Gruse (122) reported further modifications. Weinrich (151) described the development of suitable conditions of temperature, pressure, and catalyst concentration to obtain good yields of trialkylated phenols, including DBPC, by using a commercial meta- and para-cresol cut of coal tar acids and continuously separating the dibutylcresols by distillation. With Loew, Weinrich (152) cited an arrangement of a apparatus and a process for bringing phenol, in the presence of sulfuric acid or ethyl sulfate, into contact with a tertiary olefin and removing the acids and acid-forming compounds by washing with a dilute alkali above 85 ° C and under superatmospheric pressures below 125 pounds per square inch gauge. Stillson, Sawyer, and Hunt (139) have an excellent paper on the details of the preparation of DBPC and other trialkylated phenols including data on yields. Various other tri-substituted phenols have been produced (119,120,136,137) from this basic reaction.

Starting with a monohydroxy-phenolic compound such as para-hydroxybiphenyl and heating it in a mixture of isobutylene and a solution of an alkali metal sulfate or ammonium sulfate in sulfuric acid, Stevens and Nickels (128) produced alkylated phenolic compounds such as DBPC. Patents to Kluge and Knowles (59) who described the alkylation of p-chlorophenol to form 2,6-di-tert-butyl-4-chlorophenol and to Stevens and Gruse (118) who obtained dialkylcyclohexylphenols by condensation of a dialkylphenol with

a carbocyclic compound further indicates the wide range of types of compounds used to prepare antioxidants.

One other catalyst which has been successfully used recently in the alkylation of phenols with agents such as isobutylene is tetraphosphoric acid. Arvin and Hunn (5) in 1947 used it to make a mono-alkylphenol and Stillson (133) has given the details for producing DBPC from p-cresol and isobutylene employing tetraphosphoric acid.

Since the experimental part of this thesis is concerned with the oxidation of DBPC, its preparation will be given in some detail. Para-cresol is alkylated with isobutylene. The reaction is carried out at atmospheric pressure or slightly above and at 60-70° C. by vaporizing the isobutylene into a rapidly stirred solution of 5% by weight of concentrated sulfuric acid dissolved in the cresol (m.p. 36° C). The time of introducing the isobutylene can vary from several hours to a few minutes depending on the heat transfer surface available to remove the heat of reaction. Polymers of di- and tri-isobutylene form a side reaction, the amount formed depends on the time of the reaction. Excessive time may yield 10-20% polymer by weight while a reaction time of 10 minutes may give only 2-3% polymer and up to 90% product in the alkylate. Catalyst concentration can vary within narrow limits to get efficient alkylation. Less than 3% by weight lowers the degree of alkylation while greater than 5% tends to produce excessive side reactions and forms high boiling point residues.

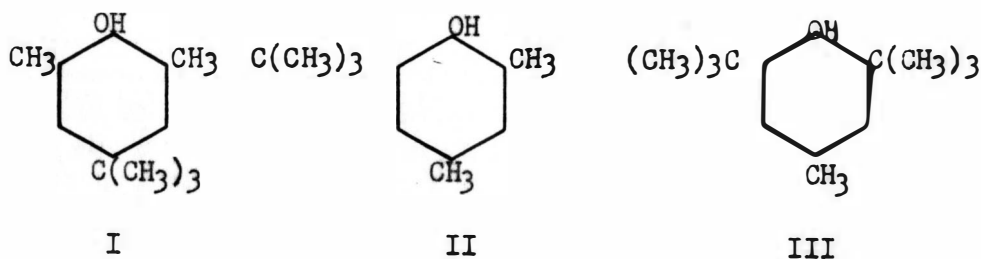
The products are separated by distillation. Extreme care must be taken to remove all acidic materials from the distillation charge whenever one or both of the ortho-positions are occupied by butyl groups or larger to prevent dealkylation and loss of the ortho substituents. Dibutyl cresol isomers can be separated by distillation as they boil approximately 20° C apart. All impurities can be eliminated in the final product by a sharp prefractionation of the cresol charge used as a starting material to make sure the para-cresol is not contaminated by any of the meta isomer.

C. Properties of the Hindered Phenols

The physical properties of the hindered phenols are quite similar to those of ordinary phenols when compared on the basis of equal molecular weights. DBPC is a white crystalline solid insoluble in water. It is soluble in petroleum ether and most organic solvents as are the ordinary phenols. Pure DBPC freezes at 70° C, boils at 265° C under 760 mm of mercury pressure and has a specific gravity of 1.048 (20°/4°). The commercial product has a flash point of 127° C. A Koppers Company, Inc., bulletin (60) summarizes other properties of DBPC and Pardee and Weinrich (94) have published pertinent physical data including methods for calculating such properties as thermal conductivity, heat of vaporization, specific heat, and heats of reaction for 60 alkylated phenols.

The chemical properties of the hindered phenols can best be studied by comparison with some of the typical chemical reactions of ordinary phenols. It has been mentioned that these substituted phenols are a class of compounds whose phenolic properties are hindered sterically by the presence of tertiary butyl or larger hydrocarbon groups in the two ortho positions. Consequently, their properties present a marked contrast to those of simple phenols such as phenol and the cresols. Table I presents such a comparison. In some instances reactions of DBPC are given as representative of its class of compounds.

It must be kept in mind that the properties of the phenols change in a more or less orderly manner as the ordinary phenols, the partially hindered phenols, and the completely hindered phenols are considered in that sequence. For example,



I is soluble in 10% NaOH while isomers II and III are not. I and II can be dissolved in Claisen solution while III cannot except that if the Claisen solution is prepared with absolute methanol III will dissolve to the extent of six grams per liter. If 90 parts methanol

Table I. Chemical Reactions of Hindered Phenols Compared to Other Phenols

Reaction	Ordinary Phenols	Hindered Phenols	Conditions to Achieve Reaction
1. Solubility in aqueous alkali solution	Readily soluble	Not soluble	
2. Solubility in alkali in absolute methanol	Readily soluble	6 g/l for DBPC	
3. Reactions with alkali metals	React readily with sodium in absolute ether	Metallic sodium has no effect on anhydrous petroleum ether or diethyl ether solutions of hindered phenols even at reflux temperatures.	Liquid ammonia solutions take up one equivalent of sodium accompanied by precipitation of the salt. Original compound can be recovered by hydrolysis. Mixture of Na-K salts can be prepared by shaking an anhydrous diethyl ether solution of hindered phenol with Na-K alloy, a liquid at ordinary temperatures (139).
4. With CH_3MgI	Liberation of one equivalent of CH_4 for each active hydrogen atom in phenol molecule	Same. (This was one of the steps in the proof of structure; that hindered phenols were true phenols and not ethers.)	

Reaction	Ordinary Phenols	Hindered Phenols	Conditions to Achieve Reaction
5. With alcoholic ferric chloride solution	Usually an intense color with practically all hydroxy-compounds	No coloration	
6. Condensation with aldehydes	Readily forms variety of condensation products including varnishes, lacquers, and synthetic resins (Bakelite, etc.)	No reaction	
7. Condensation with ethylene oxide	Forms phenoxy-ethanols and polyethylene glycols	No reaction	
8. With acetylene	Readily forms vinyl ethers	No reaction	
9. Esterification	Esters prepared directly by action of phenol and acid anhydride or acyl chlorides	Cannot be prepared by regular methods due to insolubility in aqueous and alcoholic alkali solutions.	Anhydrous petroleum ether suspension of the sodium salt formed in liquid ammonia refluxed with benzoyl chloride gives a crystalline solid. Also, treating the Na-K salt mixture mentioned in item (3) above with benzoyl chloride yields a benzoate identical with that obtained from the sodium salt formed in liquid ammonia. (139).

Reaction	Ordinary Phenols	Hindered Phenols	Conditions to Achieve Reaction
10. Nitration	Nitrates easily to from mono-, di-, and tri-nitro derivatives depending on the phenol.	Forms mono-nitro derivative in acetic acid but temperature must be kept low to prevent dealkylation and oxidation.	
11. Hydrogenation	Will hydrogenate to corresponding cyclohexanol relatively easily.	Complete hydrogenation to corresponding cyclohexanol does not appear feasible.	Will go to a substituted cyclohexanone at temperatures of 200-250° C and pressures of the order of 2500 lbs per square inch using a Raney nickel catalyst (60,153,154).
12. Physiological	Phenol is a violent poison, has a strong caustic action on the skin causing the formation of blisters, and is easily absorbed through the skin and mucous membranes. Most phenols are antiseptic.	Complete absence of burning action on the skin. Breathing vapors is somewhat disagreeable but has never resulted in ill effects even in exposures of over a period of years.	

Sulfuryl chloride produces the monochloro-derivative of DBPC, the chloride ion replacing one of the remaining hydrogen atoms on the benzene ring.

and 10 parts of water are used the solubility drops to 2.7 grams per liter (132). Phenols with isopropyl groups in the 2,6 positions are insoluble in dilute NaOH but soluble in Claisen solution.

It is difficult to say definitely whether the solubility characteristics are due to the presence of higher alkyl groups which decrease the solubility in aqueous alkali solutions generally or to the partial retardation of the phenolic properties by steric effects; both factors may be responsible. Certainly in the isomeric compounds I and II the degree of alkali insolubility appears to be greatly influenced by the position of the tertiary butyl group relative to the hydroxyl group.

Tertiary amyl groups in the two ortho-positions render the hindered phenol immune to the action of alcoholic or aqueous alkali, sodium in liquid ammonia, or to sodium-potassium alloy suspended in anhydrous ether (139).

One other reaction of hindered phenols has received considerable attention. Under the influence of alkylation type catalysts such as aluminium chloride, tetraphosphoric acid, sulfuric acid, and alkyl esters of sulfuric acid, alkylated phenols can be dealkylated to produce olefins, phenols, and various byproducts (3,31,85,124,125, 126,127,134,135). This property is made use of to separate mixtures having closely related boiling points by first alkylating, then fractionating the alkylated products, and finally dealkylating to recover the original substances (2,113,123). Smith (104) studied the transfer of some tertiary alkyl radicals from a substituted phenol

to a hydrocarbon by refluxing p-tert-butylphenol with benzene in the presence of aluminum chloride and recovering tert-butylbenzene and phenol.

Preliminary data indicate that DBPC has a low order of toxicity. Its use in foodstuffs and related materials has not been approved by the United States Department of Agriculture unless such approval has been recently granted.

These properties characterize this class of compounds called hindered phenols and show how steric hinderance effects the reactions characteristic of the hydroxyl group of phenols.

D. Detection, Separation, Purification, and Identification

A literature survey on a topic as broad as this must of necessity be incomplete. Most of the knowledge required to set up a scheme to analyze the products of a chemical reaction can be obtained from standard reference and text books in the field of qualitative and quantitative analysis. No attempt has been made to include this type of information here but rather to locate and record specialized processes and techniques which have been developed and which may be modified and adapted to use on the analysis of the products of the oxidation of a hindered phenol.

Some unreacted phenol will probably be present at the end of any oxidation experiment therefore some tests for them are listed. Also, since in further work along this line, the hindered phenol will actually be oxidized in an oil, schemes will have to be devised to separate oxidation products from hydrocarbon mixtures.

Hence, any information which may be of assistance in this operation is recorded.

It has been noted in the discussion of the properties of the hindered phenol that they do not undergo many of the normal phenolic reactions. Therefore, many of the tests listed in standard reference and text books for phenols cannot be used with this class of compounds. No review could be found which discussed the limitations of standard phenol tests as far as hindered phenols were concerned. However, two color tests have been developed which are sensitive to the presence of alkyl substituted phenols. Stillson, et al. (139) reported a spot test which detected as little as one part of 2,4,6-tri-tert-butyl-phenol in 8,500 parts of alcoholic solution. A few crystals or one drop of the sample are placed in a "spot" plate and dissolved in a few drops of 95% ethyl alcohol. A drop of 2% phosphomolybdic acid solution is added, followed by two drops of concentrated ammonium hydroxide solution. A deep blue color developed if any phenol or a hindered phenol is present.

Alkyl substituted phenols used as antioxidants in lubricating oils are detected by means of a second phosphomolybdic acid method reported by Snyder and Clark (105). The procedure is a combination of extraction and color development. Two to five grams of the oil is treated in a separatory funnel with four milliliters of phosphomolybdic acid reagent (1.2 grams in 100 milliliters of ammonium hydroxide), then eight milliliters of a mixture of 25 milliliters of concentrated ammonium hydroxide, 50 milliliters of ethylene glycol, and 50 milliliters of n-amyl alcohol, are added. After vigorous

shaking, the layers are allowed to separate (two milliliters of saturated potassium chloride helps here). A portion of the lower layer is poured into a one centimeter absorption cell and the absorption at 700 millimicrons measured after exactly 10 minutes. The blank color is obtained from a similar non-treated base oil. Different base oils give different blank colors and different phenols vary in color sensitivity. Therefore, for accurate results it is necessary to operate with a comparable base stock and know the identity of the phenol being sought.

Ware (145,146,147,148) has published considerable data on detection of phenols and perhaps some of the tests given could be developed for use with hindered phenols. Reliable and quick methods for analyzing the various distillates recovered in the fractional distillations involved in the production of the tert-butyl derivatives of cresols have been developed by Stevens and Nickels (130). Freezing points and cloud points of various binary mixtures (some of which include DBPC) are described. Friedel and Pierce (42) carried out a qualitative and quantitative analysis on a carbon disulfide solution of some alkyl phenols and phenol by means of infrared spectrometry. Deviations from Beer's law was found to be practically zero. Again there are possibilities that these methods may be modified to apply to the analysis of mixtures containing hindered phenols.

Hydrogen peroxide solutions have been used in some instances as a reagent for phenols (52,147).

Assuming that when a hindered phenol acts as an antioxidant in inhibiting the decomposition of a turbine oil or other lubricating oil, the phenol itself is oxidized, then, in the final analysis,

the oil will contain various oxidation products plus some of the unoxidized phenol. To study the mechanism of the oxidation of the hindered phenol it will be necessary to isolate and identify the various oxidation products. One of the most promising methods for recovering the unreacted antioxidant and oxidation products from petroleum oils and then for separating oxidation products involves the use of chromatographic techniques.

Williams (156) has written an excellent book on the introduction to chromatography. Background material can be gotten from other sources (20,37,45,51,68,69). Mair and co-workers (76,78,79) have done considerable work on the determination of the amount of aromatic hydrocarbons in gasoline. They percolated the mixture through a silica gel column and followed the change in the nature of the percolate by measuring the refractive index of successive samples leaving the bottom of the column. By a modification of the above they determined the aromatic and mono-olefin hydrocarbons and extended the technique to higher boiling hydrocarbons such as kerosene. Conrad (27) developed a rapid chromatographic method for determining aromatics in hydrocarbon mixtures in the gasoline-kerosene range by using a combination of silica gel separation and ultraviolet-stimulated fluorescence. The ratio of the length of the fluorescent band to the length of the entire sample determined the aromatic content. Dineen, et al. (33) used the silica gel technique to examine the naphtha derived from shale oil.

A paper by Mair (77) summarized the work done over a 15 year period on the use of adsorption as a process for separating and

analyzing hydrocarbons. He enumerated the applications of adsorption technique as follows:

1. separation of aromatics from paraffins and cycloparaffins.
2. separation of mononuclear from polynuclear aromatics.
3. separation of olefins from paraffins, cycloparaffins, and aromatics.
4. separation of paraffins from cycloparaffins.
5. separation of individual members in paraffin, cycloparaffin, and alkylbenzene classes from each other.
6. separation of polar non-hydrocarbons such as oxygen, sulfur, and nitrogen compounds from hydrocarbons.

Adsorption procedures can be applied to low molecular weight fractions of petroleum like gasoline and to high molecular weight fractions such as oils and lubricants. Mair's summary includes discussion of apparatus and materials, and examples of the application of the process.

Lipkin and co-workers (70) modified the procedure of Mair and Forziati (78) to make it applicable to higher boiling point petroleum fractions. Mills (83) used an adsorption column the top half of which was silica gel and the lower half clay to rapidly determine the amount of aromatics in oil. The oil was dissolved in n-pentane.

Williams (155) used activated alumina and petroleum spirits (b.p. range 40-60° C) to separate the oxidation products from a medium turbine oil that suddenly deposited a sludge after nine years of use. No individual oxidation products were identified. The use of chromatographic columns two inches in diameter and six feet long filled with various adsorbents such as activated silica to examine used lubricating oils from internal combustion engines was reported by Lahiri and Mardles (65).

The literature contains a number of references to the removal of phenols from hydrocarbon products. Stainer (106) extracted phenol and "other acids" from tar oils and other hydrocarbon oils with an organic base insoluble in the oil. Roos and Schwamberger (98) dephenolized liquid hydrocarbons by treating them with another liquid hydrocarbon such as crude benzene and an aqueous solution of a salt such as pyridine sulfate. The salt is readily soluble in phenols but insoluble in the hydrocarbon. Therefore, on separating the layers, phenols will be in the water layer.

Aqueous ammonia whose density had been increased by addition of some salts like lithium nitrate, calcium nitrate, or sodium chloride was used by Kerr and fellow workers (57) to extract phenols from oils, tars, etc.. The two layers were separated, the ammonia removed, and the phenols recovered. Still (131) used as solvents, ammonium salts and ammonia addition compounds which are liquid at ordinary room temperatures, to extract phenols from hydrocarbon oils. Farbenind (38) performed the same task by means of an aqueous alcoholic

(70% methyl alcohol) solution. The extracts were treated with suitable organic liquids. An almost pure phenol was separated by distillation. Newton (91) reported a method for completely removing phenols from cracked gasolines so as to prevent their acting as natural oxidation inhibitors hence influencing the induction period of the gasoline in control tests. They were made into azo-dyes and separated into an aqueous layer.

Kozacik and Sachanen (61) outlined a procedure for separating oxygen-containing materials, such as water-soluble organic acids or salts, oil-soluble organic acids and salts, and unsaponifiable organic oxygen-containing compounds from oxidized petroleum fractions. The oxidized petroleum fraction was treated with about two volumes of 10% sodium hydroxide solution for $3\frac{1}{2}$ hours at approximately 100° C. The reaction mixture separated into an aqueous layer and an oily layer. After separating, the aqueous layer was acidified with 18% hydrochloric acid and the organic acids liberated. The water-insoluble acids were separated as a layer and dried by binary distillation with benzene. The water-soluble acid layer was neutralized, evaporated to dryness, and the residue extracted with a hot 90% ethyl- 10% methyl alcohol solution. The sodium salts of the water-soluble organic acids were then obtained from the extract. The oily layer containing unsaponifiable oxygen compounds and unoxidized hydrocarbons was extracted with acetonitrile (or liquid sulfur dioxide or phenol) to separate the acetonitrile-soluble oxygen compounds from the hydrocarbons. The acetonitrile was removed by distillation.

The yields of the various fractions were given. No individual substances from the various fractions were identified.

During the period 1947 to 1951 some patents were issued for the purification of alkylphenols. The methods developed involve either special distillation techniques (6,17) or recrystallization procedures (30,100,113). Purities to 99 mole-percent were claimed by Davidson's recrystallization scheme (30). Also, during this period Nametkin and co-workers (90) published data on the identification of 154 phenols in the form of amides and anilides of phenoxyacetic acids.

This section could be expanded considerably if many standard techniques familiar to the analytical chemist for analyzing the type of mixtures encountered in this problem were included. However, these methods are generally known or readily available and so will not be reviewed here.

E. Uses of the Hindered Phenols

The outstanding use of hindered phenols and especially DBPC is as an antioxidant. Some of the mono- and dialkylphenols have properties which made them of value as insecticides, germicides, and antiseptics (88,96) but the trisubstituted derivatives are important primarily for their oxidation-inhibitory characteristics.

The effectiveness of alkylated phenols as antioxidants for lubricating oils, steam turbine oils, and other petroleum products has been recorded (35,114,119,120,136,137,138). For the

stabilization of certain specialty oils, such as transformer oil, as well as other petroleum oils the phenolic compounds may be used in admixture with such other compounds as aromatic amines, metallic phenates and alcoholates and substituted aminophenols (15,16,32,75, 141,142).

DBPC has been shown to be an excellent antioxidant for lubricating oils as it retards the formation of acids and other degradation products which can corrode metal bearings. It does not increase the rate of sludge formation nor does it have any detrimental effects on the desired physical properties of the oil. Since it is soluble in oil but insoluble in water or caustic solutions, it will remain in solution in the oil during service.

The addition of DBPC to gasoline inhibits the oxidation of certain substances which, when oxidized, form gums and color-imparting bodies which are not desirable.

Pyrethrin-containing insecticides have a marked tendency to decompose on exposure to air and light with a resultant decrease in insecticidal value of the substance. DBPC stabilizes these insecticides thus insuring their potency (103).

Wasson and Zimmer (149) describe an instrument lubricant with desirable properties whose recommended composition includes 0.5% DBPC. It also serves as an effective stabilizer and antioxidant for the synthetic lubricating fluids prepared from the esters of aliphatic acids.

A small amount of DBPC is an effective antiskinning agent for oleoresinous paints and varnishes used in baking finishes. Studies

have also shown that it is one of the most effective of the alkylated phenols as a stabilizer and antioxidant for vinyl ether polymers.

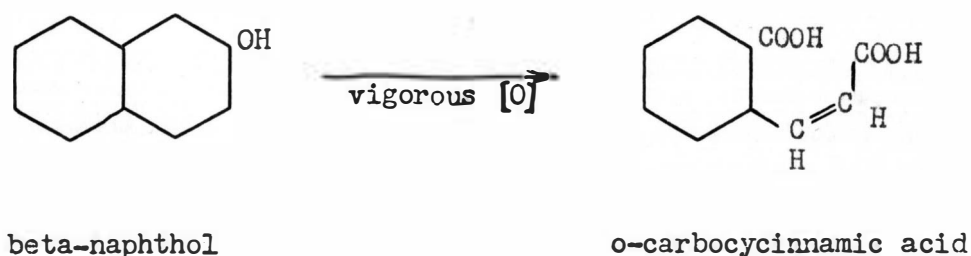
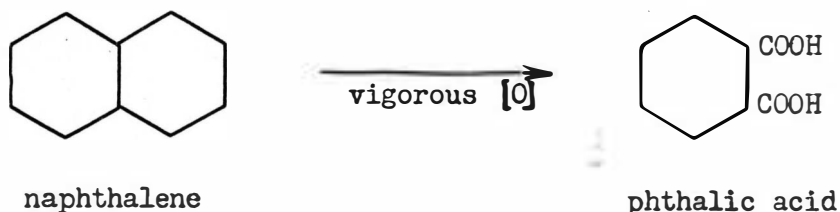
DBPC is useful as an antioxidant in white rubbers since it causes little or no discoloration even after prolonged exposure to heat, light and air. This property has suggested its use as a stabilizer of such materials as cellulosic plastic compositions, plasticizers used with polyvinyl compounds, animal fats and oils, and vegetable oils.

F. The Mechanism of Oxidation Reactions

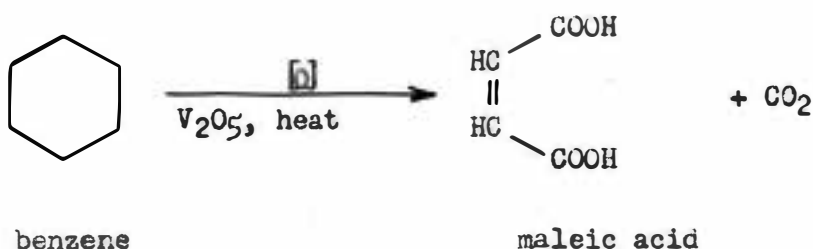
There is little evidence in the literature as to just how monohydric phenols retard, and in some instances, inhibit almost completely, the autoxidation of olefinic oils and other technically important substances. It is not known for sure whether or not they are destroyed by the oxidation reaction which takes place in their presence though available information indicates this to be the case. Most textbooks state that phenols are easily oxidized, that the oxidation products are complex, and that extensive degradation of the molecule takes place. The observed effect is the development of colored products. Even pure phenols develop color on long exposure to air at room temperature.

The stability of the benzene ring is known from the fact that side chains attached through a carbon atom to the ring can usually be destroyed down to this carbon atom which is converted to the

carboxyl group ($-\text{COOH}$) without affecting the ring. Oxidizable groups in side chains undergo normal oxidation prior to destruction of the chain itself. Naphthalene behaves towards oxidizing agents as if, at any one time, one ring was more susceptible to attack than the other. Therefore, on vigorous oxidation with potassium permanganate or with air and a catalyst, naphthalene is oxidized to phthalic acid. Similarly, beta-naphthol and permanganate or peroxyacetic acid form o-carboxycinnamic acid.

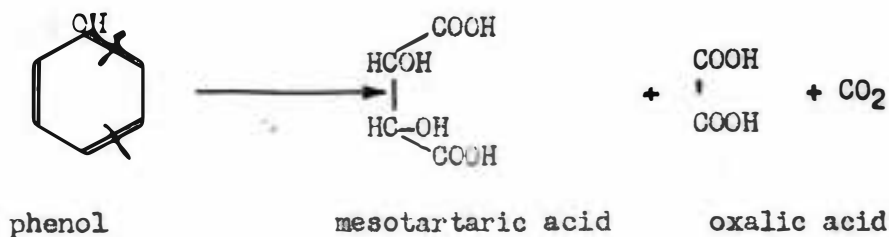


However, the oxidation of the aromatic nucleus can be carried out under proper conditions even with benzene, as evidenced by a commercial method of producing maleic acid.



Further indications of the ease of oxidation of phenols are noted by Bachman (7) in that oxidation with resultant destruction of the aromatic character of the molecule and formation of complex byproducts often accompany bromine substitution of phenols unless considerable care was exercised in the control of conditions.

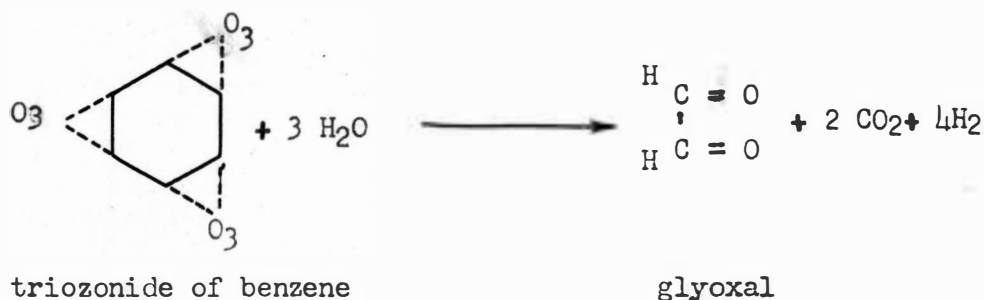
According to Beilstein (10) an oxidation experiment involving phenol and potassium permanganate in alkaline solution and at zero degrees centigrade yielded mesotartaric acid, oxalic acid and carbon dioxide.



(wavy line indicates points of ring rupture)

Gibbs (43) made an extensive study of the effect of sunlight on phenolic compounds and wrote of the reaction of ozone with phenol.

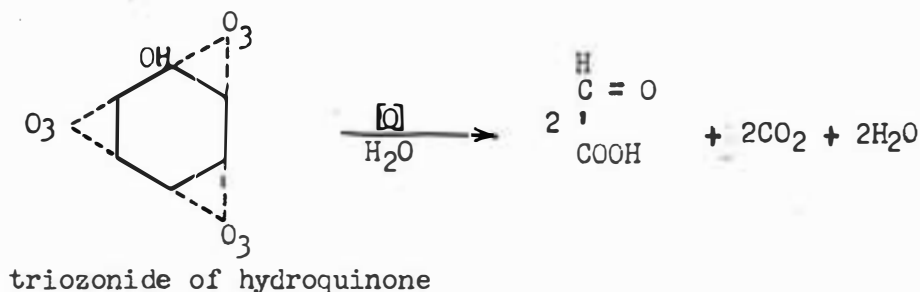
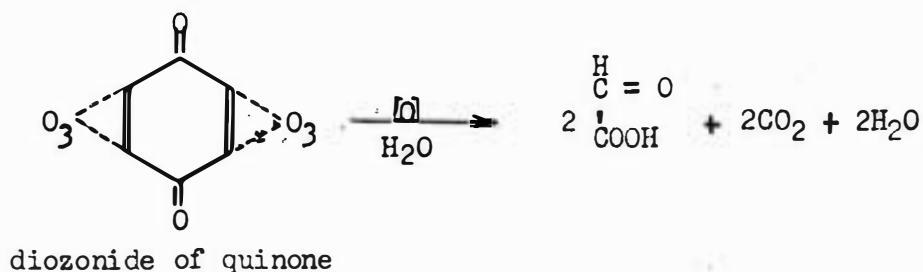
Dry ozone was, in general, not very reactive but was much more so in the presence of traces of moisture. With dry pure substances the reaction was greatly influenced by temperature. At room temperature, the first product formed was quinone and possibly some hydroquinone as indicated by the discoloration. As the reaction proceeded an ozonide was undoubtedly formed. This was indicated by the copious evolution of carbon dioxide and the formation of glyoxalic acid, a reaction analogous to the breaking down of the triozonide of benzene as demonstrated by Harries and Weiss (47).



When ozone reacted with dry phenol, the water which seemed necessary to the breaking down of the triozonide and which also accelerated the reaction, was produced during the formation of the quinone as follows:



With moist phenol, the same reaction products were produced, hydroquinone in larger quantities than quinone. Whether it is the diozonide of quinone or the triozonide of hydroquinone that breaks down according to the following reactions:

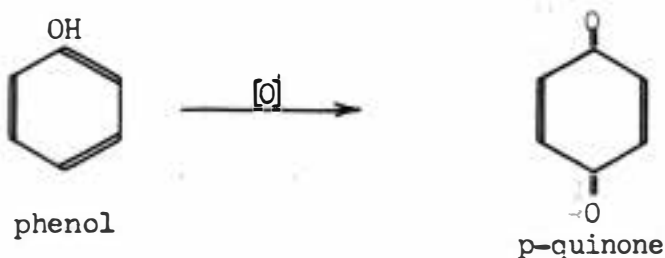
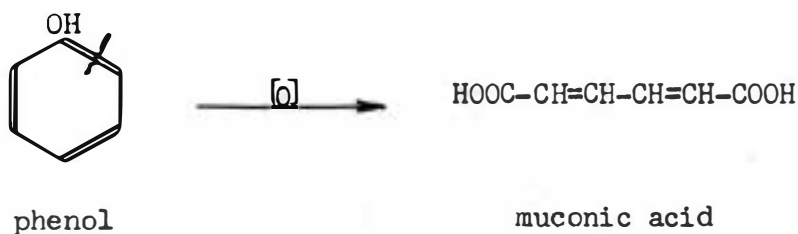


has not been determined. Later researches (56) have added the following information that the oxidation of phenol with ozone is not a chain reaction, that the presence of sulfuric acid increases the oxidation and that manganous sulfate catalyzes the reaction.

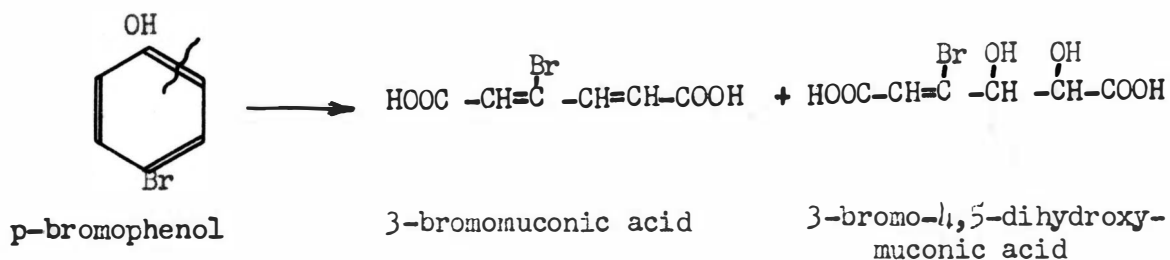
A series of experiments were made oxidizing alkyl benzenes and tertiary hydrocarbons with gaseous oxygen (109,110,111,112). Aldehydes and acids were formed with the methylbenzenes and ketones with other starting materials.

Bösesen and co-workers (11,12,13) made one of the early careful studies of the oxidation of a number of phenols with peroxyacetic acid. With ordinary phenol, ring rupture was observed

when the oxidation was directed to the ortho-carbon atom and para-quinone formed when oxidation was directed to the para-carbon atom. In the first case, muconic acid was formed.



The p-quinone reacted with unoxidized phenol to form phenoquinone. It was noted that, as byproducts, some reducing agents, probably glyoxalic acid and maleic acid were formed. It was postulated that when the first reaction occurred, i.e., attack at the carbon atom with the hydroxyl group and the adjacent ortho-carbon atom, the muconic acid was produced via o-quinone. The oxidation of catechol resulted in muconic acid, carbon dioxide and some fumaric acid. Hydroquinone formed quinhydrone and, if the mixture set for 10 days, some fumaric acid. However, p-quinone could not be formed from para-substituted phenols and the reaction was studied as a method of producing beta-substituted muconic acids. Oxidation of p-bromophenol yielded 3-bromomuconic acid and 3-bromo-4,5-dihydroxymuconic acid.



The p-chlorophenol gave a similar reaction except that the lactone of the dihydroxy acid was isolated instead of the acid. It is interesting to note the passage from aromatic to aliphatic compounds in these reactions. Other reactions were studied. No reaction took place with 2,4-dibromophenol or 2,4,6-tribromophenol.

Other investigators checked these results. Wacek (144) affected the cleavage of phenols with peroxyacetic acid in the presence of salts of iron, nickel, cobalt, sodium, calcium, mercury, zinc, copper, chromium, and manganese. Catechol gave high yields of muconic acid, p-chlorophenol formed chloromuconic acid, and p-cresol resulted in fair yields of methylmuconic acid. Chwala (24) found that the oxidation of phenol with dilute hydrogen peroxide in the presence of ferrous sulfate gave hydroquinone and catechol.

A number of interesting publications have appeared in the last few years that have furnished valuable information on oxidation reactions (28,29,55,60,71,84,102,140,150). According to the theories developed for the oxidation of oils by oxygen, the first step is the

formation of an oxide or a peroxide which then either breaks down directly into aldehydes and acids of lower molecular weight or reacts with water or other hydrocarbon molecules to form substances containing hydroxy or keto groups. Cosgrove and Waters (28) recognized autoxidation to be homolytic chain reactions involving free radical thus:



in which inhibitors (H-In) are pictured as effecting chain reactions in this manner,



where the radical, $\cdot In$, does not continue the chain sequence but becomes converted to stable molecules in some other way. They hoped to gain an insight into the role played by phenols in autoxidation reactions by studying their behavior with benzoyl peroxide, a typical radical-forming agent.

Benzoyl peroxide decomposed much more rapidly in solvents such as m-cresol which contained active hydrogen than in nonionizing solvents such as benzene. The benzoate free radical, if left unreacted, decomposed further liberating carbon dioxide. Cosgrove and Waters found that the free radical reacted with phenols at a much faster rate than that at which carbon dioxide was evolved.

In a later study, these same investigators oxidized a number of phenols with hydrogen peroxide in the presence of sulfuric acid or

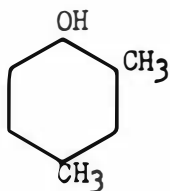
acetic acid. The following were among the results given:



(18 g.)



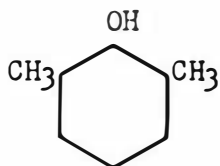
12.2 g of unreacted phenol.
0.7 g of 4a,8-dimethyl-4a-9b-dihydro-2(1H)-dibenzofuranone.
1.07 g of 2,2'-dihydroxy-5,5'-dimethyldiphenyl.



(30.5 g)



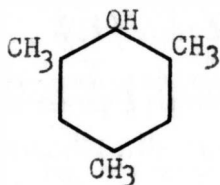
6 g of unreacted phenol.
13 g of 2,2'-dihydroxy-3,3',5,5'-tetra-methyldiphenyl.
0.2 g of a compound $C_{16}H_{18}O_2$.



(12.2 g)



6 g of unreacted phenol.
1.5 g of 3,3',5,5'-tetramethyl-4,4'-diphenylquinone.
0.8 g of 2,6-dimethylquinone.
and some 4,4'-dihydroxy-3,3',5,5'-tetra-methyldiphenyl.



(27.2 g)



8 g of unreacted phenol and the derivatives 3,3',5,5'-tetramethyl-4,4'-diacetodiphenyl and the diacetate of a diphenyl $C_{18}H_{22}O_2$.

The melting points of these compounds were given. The main reaction products were phenol dimers. Blocking the ortho-positions favors para-coupling.

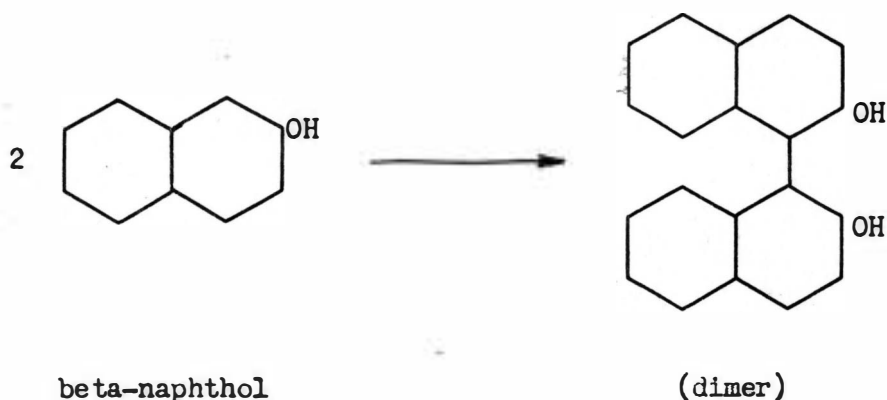
Morawetz (84) made an excellent study of the effectiveness of 34 phenolic compounds and two xylene-formaldehyde condensation products as antioxidants and established several relationships between their oxidation inhibiting efficiency and chemical structure. It was found that alkyl substitution in the ortho- and para-positions and halogen substitution on the para-position improved the stabilizing efficiency of phenolic antioxidants. Increased efficiency also resulted when an extra hydroxyl group was introduced into the molecule. The studies were made with the antioxidant added to paraffin wax at 163° C.

When paraffin wax was subjected to oxygen at elevated temperatures, no change occurred for sometime. At the end of the induction period peroxides appeared and concentration built up until fatty acids began to form at which time the peroxide concentration diminished. This peroxide formation was used to evaluate the efficiency of the antioxidants. DBPC was found to be a very good antioxidant.

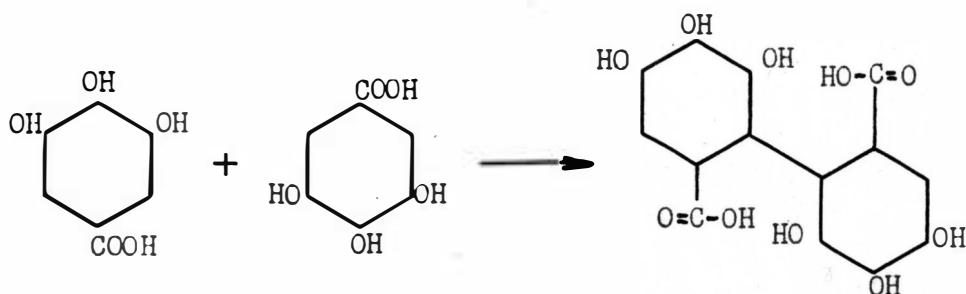
The course of the oxidation of substituted phenols was also discussed by Morawetz. Early investigators (87) believed that the antioxidant reacted with the peroxides in a series of reactions that destroyed the peroxide, the antioxidant being regenerated. Others (1) concluded that the inhibitors interrupted the oxidative chain reactions and were themselves oxidized in the process. This

latter case has been shown to be true by the studies of Böeseken, et al., discussed previously, which showed the course of the oxidation of phenols to depend on the position of the substituting group. Phenol gave muconic acid and p-quinone. Para-substituted phenols gave no p-quinone, the substituted muconic acids being formed.

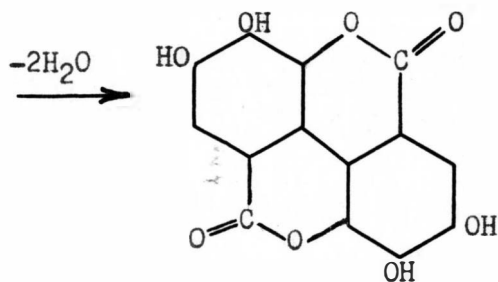
In some cases where the para-position is blocked, dimer formation was observed (8). According to Feiser (39) the oxidation of beta-naphthol with ferric chloride proceeded thus:



The formation of ellagic acid on oxidizing gallic acid followed a similar mechanism (97).



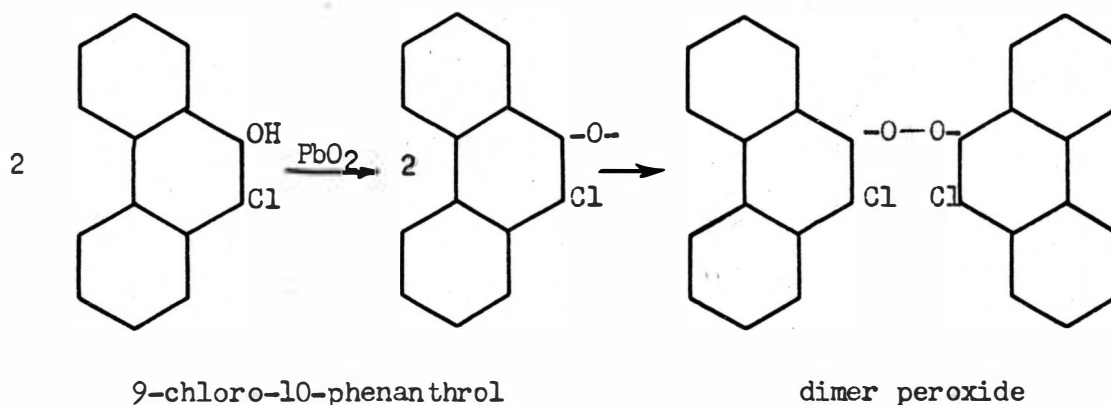
gallic acid



ellagic acid

Feiser and Feiser (40) reported an interesting phenol oxidation. The initial step in the attack of phenols by oxidizing agents is the abstraction of the hydroxyl hydrogen atom with the formation of a free radical containing univalent oxygen. Such radicals are usually so unstable and reactive that they undergo rapid transformation to other products but certain hydroxy-derivatives of phenanthrene form radicals of stability comparable to triphenylmethyl. Thanks to the investigations of Wieland, of Pummerer, and Goldschmidt, the existence of these radicals is not a question of

speculation but one of proof. The oxidation of 9-chloro-10-phenanthrol proceeds according to the following equation to form the dimer peroxide:

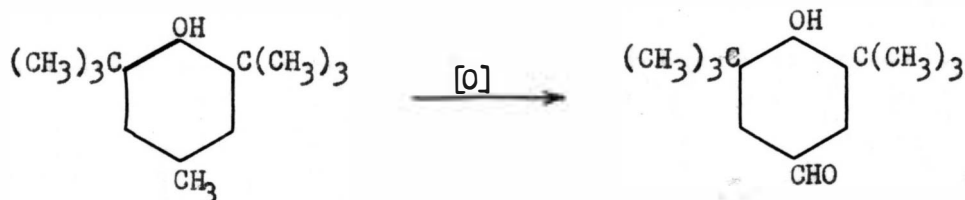


Possibly because the blocking of the positions ortho and para to the oxygen prevents a wandering of the free valence electrons to carbon atoms and because the high molecular weight retards the velocity of association, the 9-chloro-10-phenanthryl radical as far more stable than the average. It does slowly polymerize to the peroxide.

In summarizing his work on the oxidative mechanism of phenols, Morawetz stated that the increased activity of the phenols on alkylation could not be due to the oxidizability of the alkyl side chains since it was known that tertiary-butyl side chains were not susceptible to attack by oxidizing agents and para-halogen had about the same effect as para-alkyl. Also, Böeseken's studies as well as Wacek's has shown that the ring of a phenol was broken before the alkyl side chain was attacked by the organic peroxide. With mild

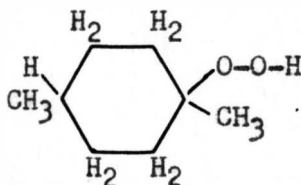
oxidizing agents, such as organic peroxides, the 2,4,6-tri-substituted phenols could undergo none of the oxidative reactions except the dimer polymerization shown by 9-chloro-10-phenanthrol reaction. The evidence would indicate that this was the reaction whereby alkyl phenol antioxidants perform their function. Blocking of the ortho- and para-positions probably prevents any undesirable side reactions with the direct oxidation of the phenol body by atmospheric oxygen. Thus, all the stabilizer is available for the reduction of peroxides in the material being protected. Unsubstituted dihydroxy phenols were ineffective as antioxidants but the alkylated derivatives were excellent. The similarity of the antioxidant characteristics of the catechol and resorcinol derivatives is additional proof that no oxidation to quinones is involved in the mechanism of the antioxidant action.

With more vigorous oxidizing agents, alkyl substituents other than the tertiary alkyls may be susceptible to oxidation. The mild oxidation of DBPC with chromic acid was reported (104). A crystalline compound melting at 185° C, assumed to be the aldehyde shown below, was obtained.



The finest paper surveyed giving details of the oxidative method and separation, recovery, and identification of oxidation products was that which reported the work of Chavanne and Bode (21) on the oxidation of 1,4-dimethylcyclohexane with oxygen. These investigators found the gaseous products carbon mon- and dioxide, methane, ethane, and hydrogen, and the liquid and solid products formic acid, acetic acid, beta-methylvaleric acid, beta-methyl-delta-acetylvaleric acid, 1,4-dimethylcyclohexan-di-ol-1,4, the stereoisomeric 1,4-dimethylcyclohexanols-1,4, and acetonylacetone (sym-diacetylthane). However, it is the experimental method rather than the results of the oxidation of 1,4-dimethylcyclohexane that is of prime importance to this study of the oxidation of hindered phenols.

In 1946, Zuidema (157) published a paper which presented a mechanism of oxidation that explained the results obtained by a number of previous investigations. Chavanne and Bode, above, had not attempted to present an explanation for the oxidative mechanism which produced the products they identified beyond postulating that the first step in the oxidation was the formation of the peroxide



Zuidema explained all the other products based on the further oxidation and decomposition of this peroxide. In discussing the works of Stephens, and Stephens and Roduta (109,110,111,112) mentioned earlier, Zuidema explained the products reported by a mechanism of formation of a peroxide at the carbon atom adjacent to the ring followed by dehydration, and further oxidation.

Larsen and co-workers (66) studied the rate of absorption of oxygen by five classes of compounds and while they did not analyze for individual compounds, they did report various functional groups present. Peroxides do not constitute a major oxidation product, although they have shown that the peroxide content rose sharply and then fell off as the oxidation progressed. Zuidema states that the free acids, alcohol, water, carbonyl, and volatile acids reported by Larsen, et al., can be explained as decomposition products and further oxidation products of peroxides and the combined acids explained by condensation reactions. Larsen, et al., found, as did Chernozhukov and Krein (22) that aromatics give condensation products which darken the oil and precipitate.

Zuidema concludes:

1. that the oxidation of a paraffin under conditions comparable to those encountered by a lubricating oil in use tends to initiate at a beta-carbon atom, that of an alkyl naphthene at a carbon atom in the ring to which an alkyl group is attached, and that of an alkyl aromatic at a carbon atom in an alkyl group adjacent to the ring.

2. that the initial oxidation product is in every case postulated to be a hydroperoxide which decomposes in one of three manners: by dehydration, by reduction with the liberation of an atom of active oxygen, or by further oxidation with the splitting of at least one C-C bond. Products can undergo further oxidation or condensation. The condensation products are especially noticable as they are usually dark and insoluble.

This literature survey brings together the important contributions of many investigators dealing with hindered phenols and related compounds and their oxidation.

III. EXPERIMENTAL

A. Objectives

The original objective of this experimental work was to investigate the products actually formed when DBPC performed its function as an antioxidant in a lubricating oil under simulated conditions of service. The complete Indiana Oxidation Test equipment was ordered and a literature survey began covering this test. However, though the equipment was ordered well ahead of the time the actual experimental work was to begin, it did not arrive, complete with accessories, until over a year later. Therefore, a change in objective was necessitated. It seemed logical to assume that when DBPC performed as an antioxidant, it itself was oxidized or suffered some other chemical change when this inhibitory action took place in its presence. Consequently, it was decided to attempt to oxidize DBPC by some standard oxidation procedure and to, as far as possible, separate, recover, and identify the products formed. This information would tend to indicate what might be expected when DBPC is used as an antioxidant in actual service. Continued investigation could conceivably lead to the development of more effective antioxidants.

B. Materials and Apparatus

The oxidative method which was decided upon was the alkaline permanganate oxidation outlined by Shriner and Fuson (101). The DBPC was obtained from Koppers Company, Inc. of Pittsburgh, Pennsylvania. Before being oxidized it was recrystallized from ethyl

alcohol.

Only ordinary laboratory apparatus was used throughout except for the chromatographic separations. Part of the chromatographic columns were made up with Merck's Alumina-Special for Chromatographic Purposes, and part with Fischer Scientific Adsorption Alumina. Commercial pentanes were used as the solvent and eluent.

C. Method of Procedure

This section includes only that experimental work pertaining directly to the permanganate oxidation of DBPC and the isolation of the oxidation products. Other work carried out during the period covered by this investigation gave no usable data and are not reported.

A number of small scale preliminary oxidations were made to experiment with separation methods. An oxidation was then made following the procedure given by Shriner and Fuson (101) with all quantities increased forty-fold. A six-liter flask was charged with 40 grams of freshly recrystallized DBPC, 160 grams of chemically pure potassium permanganate, 3200 milliliters of water, and 19 milliliters of six normal sodium hydroxide and refluxed for five hours and 20 minutes. A water vapor trap and two tared U-tubes filled with ascarite were attached to the reflux condenser to absorb any carbon dioxide that might escape from the reaction vessel. An untared U-tube of ascarite protected the tared U-tubes from any carbon dioxide from the air. The tared U-tubes showed a negligible increase in weight

(0.07 grams) which would be expected as any carbon dioxide formed would remain in the alkaline solution.

The alkaline reaction mixture was saturated with sodium chloride and extracted with ethyl ether. The ethereal solution had a beautiful red color and contained the alkaline and neutral oxidation products including the unreacted phenol. This ether solution was designated E_n. The alkaline aqueous solution contained the salts of any acid formed plus the oxides of manganese which resulted from the reduction of the permanganate and any other solids. It was filtered to remove the solids, the filtrate being clear and water-white. This filtrate was acidified with sulfuric acid and again ether extracted. A carbon dioxide collecting train was set up on the reaction vessel before it was acidified since if carbon dioxide was an oxidation product, it would be evolved when the alkaline solution was acidified. A water trap was put in the train ahead of the tared U-tubes of ascarite and, again, an untared U-tube of ascarite kept any carbon dioxide of the air from reaching the tared tubes. A total of 5.205 grams of carbon dioxide was evolved as the solution was acidified. Checks were made to make sure no significant part of this 5.205 grams could be due to ether evolved as the acid was added.

The acidified solution was then ether extracted. This ether solution was distilled to remove the ether and 2-3 grams of a very viscous, dark red residue recovered. (In a preliminary experiment, a semi-micro distillation of the ether solution at this point gave

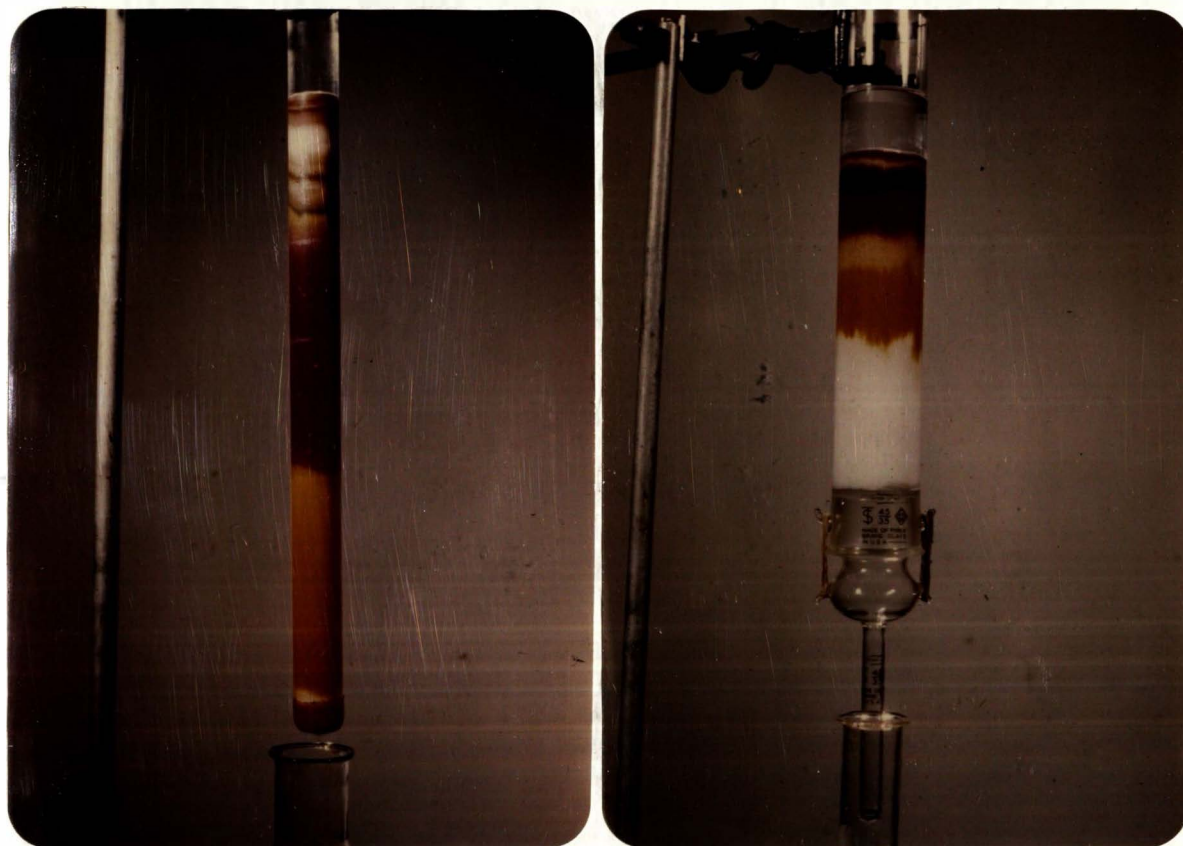
about 0.3 milliliters of a liquid with a sharp, penetrating, goaty odor which distilled over at 110° C and had a melting point between 20 and 25° C. The accuracy of the distillation temperature was questionable. This residue was dissolved in hot alcohol and a little warm water added in an attempt to bring about a crystallization of some of the material. However, when the water was added, the material seemed to condense or polymerize leaving a dark red gummy mass which became quite hard. No further attempt was made to identify products in this fraction. The acidic solution was concentrated by taking small portions, 200-300 milliliters, and distilling under vacuum. This was a tedious operation because of the large amount of sodium chloride present which had been added to "salt-out" the ether during extractions. After concentrating part of the acid solution, it was suggested that the solution be made alkaline to prevent loss of any volatile acid material. This was done and the remainder of the material concentrated thus.

The ether solution, E₁₁, from the extraction of the original alkaline reaction mixture was treated with anhydrous potassium sulfate, the hydrated sulfate filtered off and the ether removed by distillation under about 300 mm of mercury. The residue weighed 20.1 grams.

While doing preliminary oxidations, considerable study had been made of chromatographic separation techniques. A number of adsorbents and solvents were investigated. Merck's Alumina-Special for Chromatographic Purposes, and commercial pentanes seemed to be the most

promising combination for use here. However, the supply of the Merck product was nearly exhausted and on reorder some Fischer Scientific Adsorption Alumina was received instead. It seemed inferior to the Merck Alumina. It was finally decided to make up one column using the remainder of the Merck material and a second column with the Fischer product. The Merck column was 22 mm in diameter and 30.5 cm long. The Fischer column was a little larger in diameter and not quite so long.

To make up the load for the chromatographic columns, the 20.1 grams of residue from the E_n ether solution was dissolved in 500 milliliters of commercial pentanes. A residue remained which would not dissolve and was filtered off, washed with pentanes, and dried. This residue consisted of nice bright orange crystals that looked homogeneous enough to assume that they constituted a single substance. They weighed 1.28 grams and were designated compound A. They melted at 238-240° C. The pentane solution was divided into two equal portions, one loaded on the Merck column (labeled column I and the other on the Fischer column (labeled column II). Figure I shows the two columns. Column I has been partially developed by eluting with commercial pentanes but column II had just been loaded a few minutes prior to the time the photographs were taken. The layers passed down through column II much more rapidly than those on column I. The column II layers were difficult to separate as the boundaries were not sharp so most of the subsequent work was done with the products separated from column I. The bright yellowish band



(a)

(b)

Fig. 1. Two columns loaded with equivalent commercial pentane solutions. (a) Column I packed with Merck alumina and (b) column II packed with Fischer Scientific alumina.

of column I was eluted through the column, the solution was distilled, and 1.32 grams of orange crystals obtained. They were designated compound B and after recrystallization from alcohol had a melting point of 238-242° C. They appeared to be the same substance as compound A. Table II shows the results of solubility tests on compounds A and B.

Table II. Comparison of Solubility Tests Made on Compounds A and B.

Solvent	Compound A	Compound B
Water	Insoluble	Insoluble
5% NaOH	Insoluble	Insoluble
5% HCl	Insoluble	Insoluble
Conc. H_2SO_4	Soluble, reaction took place leaving the solution a deep bright red color	Soluble, reacts like compound A
Sirupy H_3PO_4	Insoluble	Insoluble

This is further evidence that the two compounds are the same substance.

After consideration of the original hindered phenol and the color, solubility tests, and melting points of A and B, it was suggested that they might be 2,6-di-tert-butyl-1,4-benzoquinone. Therefore, compound A was refluxed with hydroxylamine in pyridine solution, a test which should form an oxime with a quinone. The reaction proceeded slowly. The solution was filtered while hot,

diluted with hot water until solution just became cloudy, and allowed to cool. A good yield of crystals resulted. They were filtered off, recrystallized from alcohol, and dried. They melted at 153-154° C. However, sodium fusions and subsequent qualitative tests (23) failed to indicate the presence of nitrogen. Therefore, one could not conclude that an oxime was formed. Compound B reacted similarly.

Compound B gave a positive test with phenylhydrazine indicating the presence of the carbonyl group. An attempt was made to prepare a derivative of compound B according to McElvain (72) but using phenylhydrazine instead of nitrophenylhydrazine. Glacial acetic acid was added to catalyze the reaction. The reaction proceeded smoothly and a nice yield of light yellow crystals recovered. They were recrystallized from alcohol. The procedure was repeated using compound A with similar results. The derivatives appeared to be identical. The melting point of the compound A derivative was 206-208° C, of the compound B derivative, 225-227, of a mixture of the two, 208-211°. Compound A would be less pure than B because of the manner in which it was recovered.

No further time was available for continued investigation when this point was reached. Therefore a halt had to be called at this incomplete stage. (Approximately a year of laboratory and library work had been done which was related directly or indirectly to this problem before the major part of the work reported in this thesis was started.) However, compound B was sent to the DuGood

Chemical Laboratories, St. Louis, Missouri, for microanalysis.

The following analysis was obtained:

<u>Item</u>	<u>1st Sample</u>	<u>2nd Sample</u>	<u>Average</u>
% carbon	82.86	82.97	82.92
% hydrogen	10.54	10.72	10.63
% oxygen (by diff.)	6.60	6.31	6.46
Molecular weight	392	394	393

IV. DISCUSSION OF EXPERIMENTAL RESULTS

These facts result from this investigation:

1. The DBPC was oxidized in the alkaline permanganate solution.
2. When 40 grams of DBPC was oxidized, there was formed 5.205 grams of carbon dioxide. This indicated extensive degradation of the molecule.

3. A chromatographic separation of the residue recovered from the ether extraction of the original alkaline reaction mixture indicated that there were a number of oxidation products, i.e. there were a number of distinct layers visible on the chromatographic column.

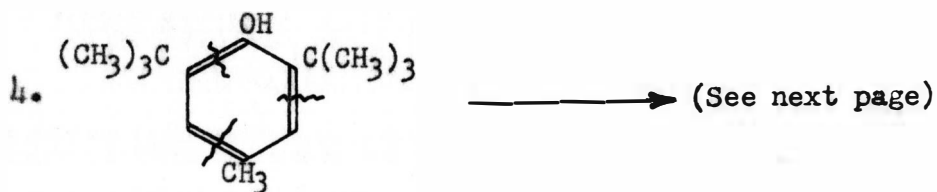
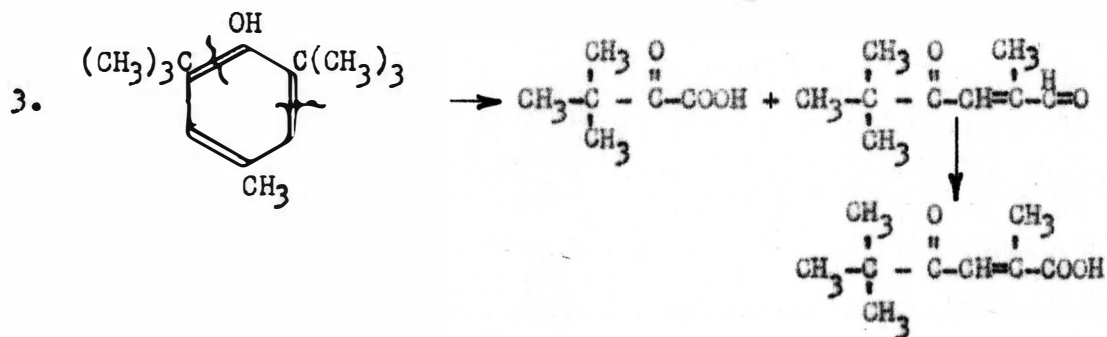
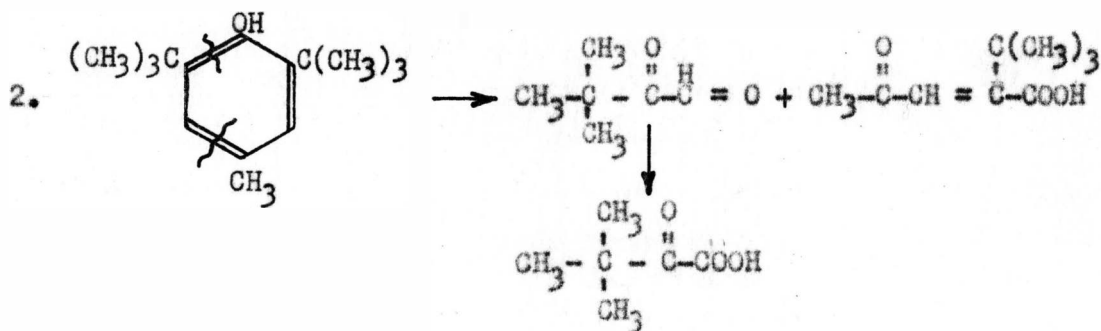
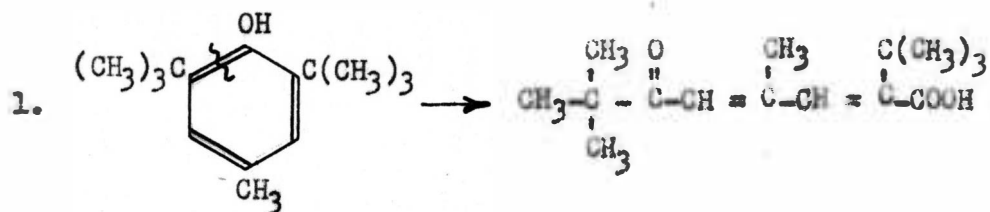
4. As a result of the above chromatographic separation, a product (designated compound A-B, assuming A and B are the same) believed to be quite pure was obtained. It reacted with hydroxylamine hydrochloride, though the resultant derivative gave no nitrogen qualitative test, and with phenylhydrazine. Compound A-B was insoluble in water, 5% sodium hydroxide, 5% hydrochloric acid, sirupy phosphoric acid, but was soluble in concentrated sulfuric acid. Microanalysis showed that it averaged 82.92% carbon, 10.63% hydrogen, 6.46% oxygen and had a molecular weight of 393.

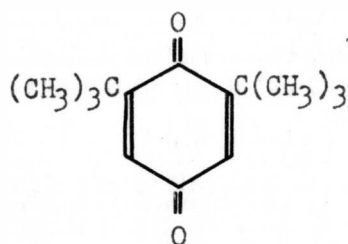
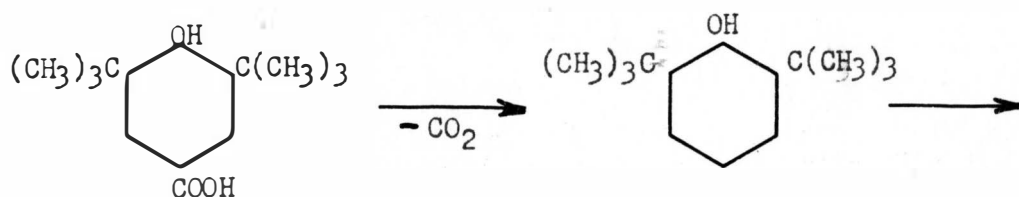
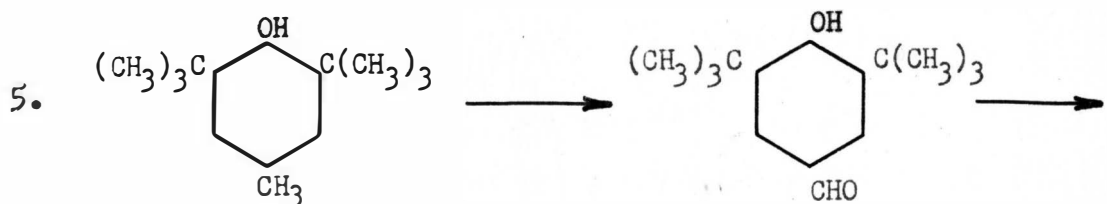
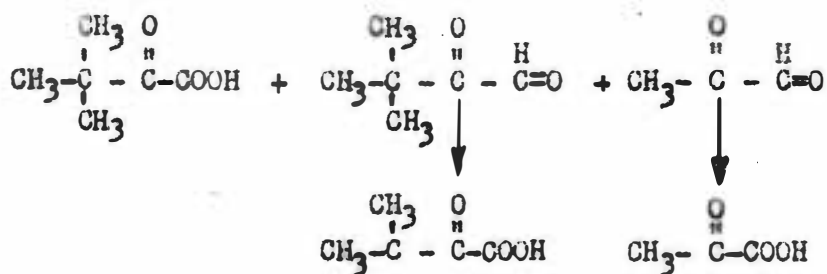
5. Other oxidation products were indicated by the fact that after the water solution resulting from the ether extraction of the original alkaline reaction mixture was acidified and again ether extracted, both the ethereal solution and the water layer had other materials present. The ethereal solution was distilled and when an

attempt was made to recover crystals from the residue, the mass seemed to condense or polymerize. (At this point in a preliminary experiment, a semimicro-distillation of the residue after removal of the ether yielded a small amount of a substance which had a sharp, penetrating, goaty odor, a melting point between 20 and 25° C, and a distillation temperature of about 110°.) The water layer, when vacuum distilled, indicated the presence of oxidation products by odor.

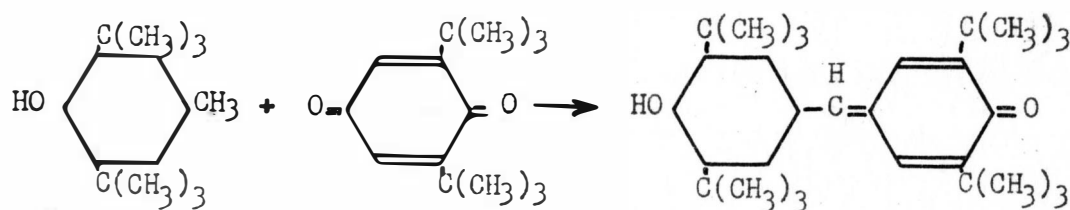
Therefore, two definite oxidation products were obtained, namely, carbon dioxide and compound A-B, many others were formed, and considerable degradation of the DBPC molecule occurred.

Speculation as to what might have happened to the DBPC molecule when it was subjected to an alkaline permanganate oxidation leads to the conclusion that a large number of oxidation products were produced. Bieseken and co-workers (11,12,13) have shown that with peroxyacetic acid, phenols suffered ring rupture with the formation of muconic acid and that with the para-position open, a 1,4 quinone could be formed. Under the more vigorous oxidizing conditions of the hot alkaline permanganate solution, it is not inconceivable that one, two, and even all three of the double bonds in the ring may have been attacked and perhaps the methyl group in the para-position as well. The following equations indicate some of the possible reactions. (Wavy line represents point of possible ring rupture.)



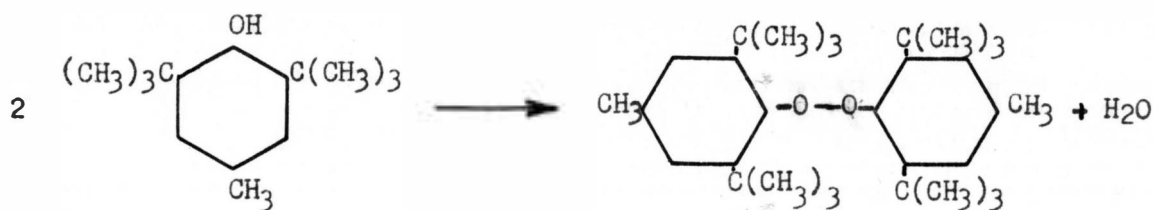


The possibility of polymerization and condensation exists and when attempting to theorize on the identity of compound A-B, the above quinone may condense with a molecule of the unreacted phenol to give a molecule like



for which carbon = 82.46%, oxygen = 7.58%, hydrogen = 9.95% and for which the molecular weight is 422. These values are fairly close to those obtained by the DuGood laboratory.

Another possibility as to the nature of compound A-B is suggested by Feiser and Feiser's (40) discussion of the oxidation of 9-chloro-10-phenanthrol. If the first step in the oxidation of DBPC is the abstraction of the hydroxyl hydrogen, the free radical formed could be expected to be quite stable because the blocking of the ortho- and para-positions prevents the wandering of free valence electrons and the relatively high molecular weight would somewhat retard the velocity of association. Therefore, it could slowly polymerize to the dimer peroxide according to the equation



for which carbon = 82.19%, oxygen = 7.31%, hydrogen = 10.50% and the molecular weight = 438. These percentages still more closely approximate those obtained by the DuGood laboratory and the reaction looks feasible. This dimer peroxide might account for the way compound A-B reacted with hydroxylamine hydrochloride and phenylhydrazine. These two substances may have been oxidized by the peroxide with the liberation of nitrogen, hence, no positive test would be possible when the reaction products were fused with sodium and tested qualitatively for nitrogen.

Reaction (5) plus further oxidation of some of the products of reactions (1) through (4) could account for the carbon dioxide recovered. Those acids which have two hydrogen atoms on the alpha carbon atom replaced by the very negative oxygen ought to be especially susceptible to decarboxylation.

The use of chromatographic methods for separating complex mixtures was especially encouraging. Further work with adsorbents and solvents may make this technique still more effective.

V. SUMMARY

In this thesis a quite complete survey of the literature concerned with hindered phenols has been given. An oxidation of a typical hindered phenol was accomplished by an alkaline permanganate method and a scheme developed for isolating and recovering some of the oxidation products. Included therein was the application of chromatographic techniques. Carbon dioxide was one of the products of the oxidation. A second product was separated and partially identified and argument presented in an attempt to explain its possible structure.

It is hoped that the groundwork has been laid which will aid in a systematic continuation of the investigation of this problem. Once a workable procedure has been formulated a number of additional oxidations can be made and the results correlated to throw new light on the mechanism of the oxidation of these compounds. This information may suggest the synthesis of improved antioxidants.

VI. RECOMMENDATIONS FOR FURTHER STUDY

This study has shown where the methods could be improved to be more effective. It is recommended that in future work, considerably larger quantities of the phenol be oxidized to insure sufficient amounts of the oxidation products so that they may be identified by ordinary macrochemical methods. A half a kilogram, or even more, may be used. Large chromatographic columns could be made to handle portions of the separations. Their effectiveness could be increased by using a large column for the crude mixture and collecting fractions which could be further purified by passing them through smaller secondary columns.

An attempt should be made to keep material weight balances to account for the total phenol in the oxidation products.

Finally, the paper of Chavanne and Bode (21) should be carefully studied as a guide to methods for separating and identifying the products formed in the oxidation.

VII. ACKNOWLEDGMENTS

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