oxide was precipitated as barium carbonate and weighed. The yield of carbon dioxide amounted to from 0.6 to 0.8 mole per mole of acid or isocyanate, corresponding to varying ratios of reaction according to equations (1) and (2).[10] The residue in the reaction vessel was filtered and the residue extracted with hot ether and hot benzene to remove the anhydride, any unreacted acid and isocyanate and the substituted amide. The residual substituted urea was recrystallized several times from alcohol in the case of carbanilide or glacial acetic acid in the case of 4,4'-dibromocarbanilide. The filtrate containing the amide was extracted with 10% sodium carbonate solution and the organic layer evaporated to dryness. The resulting crude amide was recrystallized several times from a suitable solvent. In all cases the melting points of the purified products agreed with the literature values as shown in Table II. Samples of the substituted amide and urea and of the labeled acids and anhydride used were quantitatively oxidized to carbon dioxide by a wet combustion procedure.[11] The carbon dioxide was absorbed in sodium hydroxide and precipitated as barium carbonate. All samples were counted as barium carbonate plates using an internal flow counter[12] operated in the Geiger region. Appropriate corrections were made for self-absorption. The geometry of the counting system was established by counting barium carbonate plates prepared from a National Bureau of Standards sodium carbonate-C^{14} sample of known disintegration rate. The specific activity of the barium carbonate from each of the reactants and products is given in Table II.

Acknowledgments.—The author wishes to acknowledge an interesting discussion with Dr. S. H. Lee at the inception of this work, and the help of Mr. R. Childers and Mr. W. Carrick in the preparation of some of the radioactive compounds and in some of the preliminary experiments.

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(10) If the reaction vessel was heated to about 135° and the reaction continued, the yield of carbon dioxide calculated from equation (1) became practically quantitative. This is undoubtedly due to the further reaction of the anhydride and substituted urea mentioned above.

(11) A. Fry, B. M. Tolbert and M. Calvin, University of California Radiation Laboratory Report, UCRL 1570 (1951).

(12) P. Damon, *Rev. Sci. Instruments*, **22**, 587 (1951).

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Coal Oxidation. Comparative Studies on Phenols[1]

BY G. R. YOHE, D. R. HILL, J. E. DUNBAR AND F. M. SCHEIDT

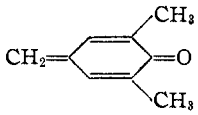
RECEIVED JANUARY 17, 1953

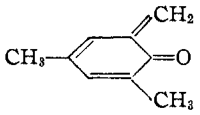
Twelve phenols were subjected to oxidation with gaseous oxygen in the presence of aqueous sodium hydroxide under conditions previously applied to coals. Oxygen absorption rate curves are shown, and compared with curves obtained from coals. A study of the oxidation products shows that oxidative condensations as well as degradations have occurred; 3,5,3',5'-tetra-*t*-butyl-4,4'-dihydroxy-1,2-diphenylethane and 3,5,3',5'-tetra-*t*-butylstilbene-4,4'-quinone were identified as alkali-insoluble oxidation products of 2,6-di-*t*-butyl-4-methylphenol. It is suggested that such oxidative condensations may play a part in the formation of "humic acids" when coals are oxidized.

In a study of the effect of methylation with dimethyl sulfate on the oxidation characteristics of coals, evidence was obtained which indicated that coals up to and including the high-volatile bituminous ranks contain appreciable amounts of phenolic structure.[2] Application of the same oxidation procedure to various types of pure organic compounds showed that the oxygen absorption rate curves for certain phenols resembled those of the coals.

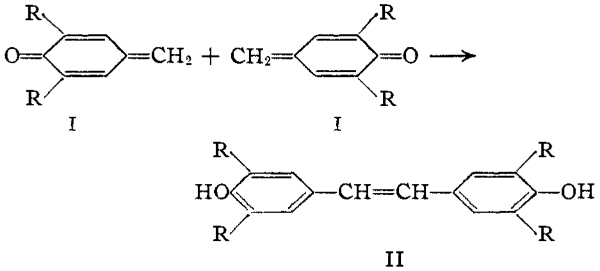
The present paper reports the results obtained by the oxidation of twelve phenols under the same experimental conditions, and includes a detailed study of the alkali-insoluble oxidation products from 2,6-di-*t*-butyl-4-methylphenol.

The possibility that the oxidation of phenols might proceed by way of quinones was considered, yet early in the work it was found that certain of the alkyl substituted phenols oxidized more rapidly than did phenol itself. The fact that simple quinones could not be formed in all cases (*i.e.*, the 2,4,6-trialkylphenols) unless dealkylation occurred first led to the suggestion that intermediates of the methylene quinone type[3] might be involved.


I


Ia

Attempts to isolate simple methylene quinones have not been successful, but have led to di- or trimeric products.[4-7] The dimerization of 4-methylene quinones (I) has been depicted[6] as a direct combination to form the dihydroxystilbene (II, R = CH_3)


II

but v. Euler[8] concluded that a disproportionation occurred forming the stilbenequinone (III) and the diphenylethane derivative IV (R = CH_3)

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(1) Presented before the Division of Gas and Fuel Chemistry, American Chemical Society, Atlantic City, N. J., September 15, 1952. Published with permission of the Chief, Illinois State Geological Survey.

(2) G. R. Yohe and Eva O. Blodgett, THIS JOURNAL, **69**, 2644 (1947).

(3) An excellent summary and review of the literature on methylene quinones has been published in "Chemie der Phenolharze," by K. Hultzsch, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1950, Chapter V, pp. 63-87.

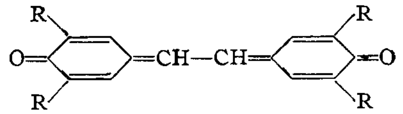
(4) T. Pummerer and E. Cherbuliez, *Ber.*, **52**, 1392 (1919).

(5) K. Fries and E. Brandes, *Ann.*, **542**, 48 (1939).

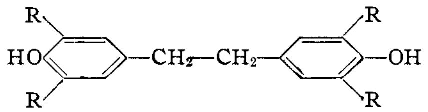
(6) K. Hultzsch, *Ber.*, **74**, 898 (1941).

(7) K. Fries and K. Kann, *Ann.*, **353**, 335 (1907).

(8) H. v. Euler, E. Adler, J. O. Cedwall and O. Törngren, *Arkiv Kemi, Mineral. Geol.*, **15A**, No. 11, 1 (1942).



III



IV

The stilbenequinone III (R = CH_3) has been prepared from mesitol by oxidation with silver oxide in benzene[9,10] and with benzoyl peroxide.[11]

In order to determine whether this type of oxidative condensation could occur with phenols under the present conditions, more detailed studies were made with 2,6-di-*t*-butyl-4-methylphenol. This compound was selected because the *t*-butyl groups in the 2- and 6-positions could not take part in methylene quinone formation, and the reaction product should be free from the analogs of III and IV having the oxygen function ortho to the 2-carbon chain connecting the quinone or benzene rings. The alkali-insoluble portion of the oxidation product was found to contain both III and IV,[12] although not in equimolecular quantities as would be expected as a result of the disproportionation mentioned above.

While this work was in progress, Cosgrove and Waters[11] reported the isolation of III from the benzoyl peroxide oxidation of 2,6-di-*t*-butyl-4-methylphenol; they did not report finding IV. A repetition of their work in this Laboratory resulted in the formation of both III and IV in approximately equal amounts.

A quite different type of product results from the oxidation of 2,6-di-*t*-butyl-4-methylphenol with *t*-butyl hydroperoxide.[13]

The relationship between III and IV was established by oxidizing IV to III with benzoyl peroxide and by reducing III to IV with lithium aluminum hydride. The identity of IV was demonstrated by analysis and by dealkylation in the presence of a trace of sulfuric acid to give IV (R = H); the latter was synthesized from 4-nitrotoluene[14–16] and from anisoin,[17] and the identity of the samples proved by melting points of their mixtures.

Alkali-soluble products are also formed in the oxidation of 2,6-di-*t*-butyl-4-methylphenol; these are being investigated.

Experimental

Materials.—The phenols used were purchased as pure compounds or were purified by recrystallization or by conversion to crystalline esters such as the acetates or benzoates. In two cases (4-*n*-butylphenyl benzoate and 1-naphthyl acetate) the ester, rather than the free phenol was charged to the reaction vessel; hydrolysis was rapid and apparently had no influence on the oxidation of the phenol.

Apparatus and Procedure.—The method and apparatus used have been described previously[2]; the reaction vessel was charged with 0.025 to 0.03 mole of phenol and 250 ml. of 5% sodium hydroxide solution. Oxygen absorption rate curves are given in Figs. 1 to 3.

Examination of Products.—Carbon dioxide and oxalic acid were determined by standard analytical procedures; the carbon dioxide was corrected for the carbonate contained in the sodium hydroxide solution used.

"Humic acid" refers to the alkali-soluble product which was precipitated as a dark brown flocculent precipitate upon acidification with mineral acid.

The volatile water-soluble acids were subjected to the Duclaux distillation procedure, and in most cases gave results which checked with prepared mixtures of formic and acetic acids. The presence of formic acid was further confirmed by the reduction of mercuric chloride; trimethylacetic acid was identified by the Duclaux method.[18]

The alkali-insoluble products from the oxidation of the naphthols were yellow, finely crystalline, and almost insoluble in common organic solvents. They failed to melt up to 400°, but partially sublimed with some decomposition. They were recrystallized by prolonged Soxhlet extraction with acetone, whereby crystals slowly accumulated in the boiling flask. Solubility behavior indicated that they were of a quinone type. Attempts to determine molecular weights were not successful because of low solubility.

The identification of the alkali-insoluble products from the oxidation of 2,6-di-*t*-butyl-4-methylphenol is treated in detail below.

The results of examination of the oxidation products are summarized in Table I.

TABLE I

OXIDATION PRODUCTS

Notes: Plus and minus signs indicate results of qualitative tests; blank spaces indicate that tests were not made.

Phenol	Time, days	Per mole of compd. CO_2, mole	$(CO_2H)_2$, mole	"Humic acid"	HCO_2H	HOAc	Other
Phenol	23	0.8	0.29				
2-Methylphenol	23	1.5	0.23	+	+	+	
3-Methylphenol	25	1.0	0.31	+	+	+	
4-Methylphenol	22	1.4	0.18	+	+	+	
Mesitol	24	2.3	0.3	+[a]	+	+	
4-*t*-Butylphenol	22	1.0	0.01	+[a]	?	+?	[b]
2,6-Di-*t*-butyl-4-methylphenol	21	–					[b,c]
2,4,6-Tri-*t*-butylphenol	21				+	+?	[b]
1-Naphthol	21	+		+			[d]
1-Naphthol[e]	22	1.3	–	+	–	–[f]	[d]
2-Naphthol	21	+		+			[d]

[a] Amount isolated, 0.1 g. [b] Trimethylacetic acid. [c] 3,5,3′,5′-Tetra-*t*-butylstilbene-4,4′-quinone and 3,5,3′,5′-tetra-*t*-butyl-4,4′-dihydroxy-1,2-diphenylethane. [d] Yellow, insoluble, high-melting polyquinone (?) [e] Charged to the reaction vessel as the acetate. [f] The amount of acetic acid was equal, within experimental error, to that resulting from saponification of the ester.

Oxidation of 2,6-Di-*t*-butyl-4-methylphenol. A. Small Batch Runs.—The combined alkali-insoluble products from three runs of 0.03 mole each weighed 10.5 g. Repeated extraction with ethanol left an orange residue which after several recrystallizations from benzene and finally from glacial acetic acid yielded 3,5,3′,5′-tetra-*t*-butylstilbene-4,4′-quinone (III), red rodlets, m.p.[19] 310–311° (Cosgrove and Waters[11] reported 300°).

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[9] C. W. Porter and F. H. Thurber, THIS JOURNAL, **43**, 1194 (1921).

[10] S. Goldschmidt and H. Bernard, *Ber.*, **56B**. 1963 (1923).

[11] S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.* (*London*), 388 (1951).

[12] Unless otherwise indicated, R will henceforth represent the *t*-butyl group.

[13] T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 (1952).

[14] A. G. Green, A. H. Davies and R. S. Horsfall, *J. Chem. Soc.*, **91**, 2076 (1907).

[15] A. Stelling and R. Fittig, *Ann.*, **137**, 262 (1866).

[16] K. Heumann and J. Wiernik, *Ber.*, **20**, 909 (1887).

[17] E. M. Richardson and E. E. Reid, THIS JOURNAL, **62**, 413 (1940).

[18] G. R. Yohe and Myra W. Lansford, *Trans. Illinois State Acad. Sci.*, **45**, 59 (1952).

[19] Melting points are not corrected for stem exposure.

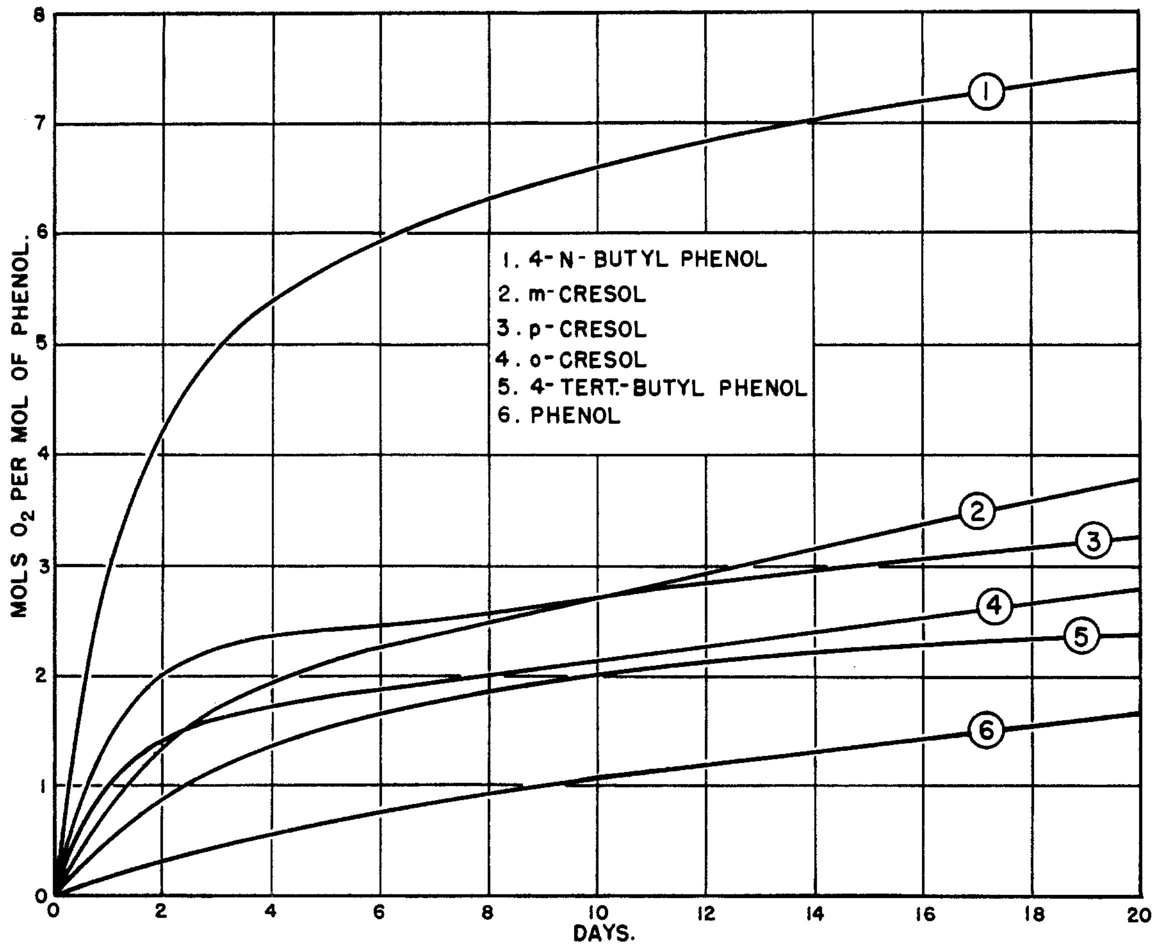

Fig. 1.—Oxidation of monosubstituted phenols.

Anal. Calcd. for $C_{30}H_{42}O_2$: C, 82.90; H, 9.74; mol. wt., 434.64. Found[20]: C, 82.7; H, 9.6; mol. wt., 433 (average of three determinations).

The ethanol extracts and mother liquors from the recrystallization of III yielded a yellow solid which after repeated recrystallization from ethanol retained the yellow color and melted at 169.5–171°; even after being chromatographed through talc and recrystallized from ethanol and water it was yellow. After ten recrystallizations from dioxane it yielded pure 3,5,3',5'-tetra-*t*-butyl-4,4'-dihydroxy-1,2-diphenylethane (IV), white, m.p. 170–171°. IV retained dioxane tenaciously and required vacuum drying at 100° for an hour to remove the solvent completely.

Anal. Calcd. for $C_{30}H_{46}O_2$: C, 82.13; H, 10.57. Found: C, 81.9; H, 10.5.

B. **Large Batch Oxidation.**—A mixture of six liters of water, 500 g. of sodium hydroxide and 300 g. of 2,6-di-*t*-butyl-4-methylphenol was stirred and heated to 90° in a stainless steel vessel and subjected to the action of gaseous oxygen under pressure of 8 cm. of water for 41 hours. The reaction mixture was extracted with petroleum ether, the solvent distilled off and the extract steam distilled to remove unchanged original phenol and the red solid residue (68 g.) recrystallized from acetone, giving 21.1 g. of an orange solid melting at 169–230°; cooling the mother liquors in an ice-bath yielded 15.8 g. of additional orange solid melting at 157–172°. Repeated recrystallization of these fractions from dioxane and vacuum drying at 100° gave 30.7 g. of IV, white, m.p. 170–171°. Fractional crystallization from acetic acid of the residues obtained from the dioxane liquors yielded 1 g. of crude III, red rodlets, m.p. 300°.

C. **Benzoyl Peroxide Oxidation.**—Following the procedure of Cosgrove and Waters,[11] two runs using a total of 23.4 g. (0.106 mole) of 2,6-di-*t*-butyl-4-methylphenol were made. The combined residues from ether trituration of the products, after recrystallization from glacial acetic acid, yielded 4.0 g. of the stilbene quinone III. Evaporation of the ether solution, recrystallization from acetic acid, ethanol, and finally ten times from dioxane gave 2.5 g. of the diphenylethane derivative IV.

Oxidation of 3,5,3',5'-Tetra-*t*-butyl-4,4'-dihydroxy-1,2-diphenylethane.—One gram of IV and 1.7 g. of benzoyl peroxide in 25 ml. of chloroform were refluxed 66 hours, washed with sodium carbonate solution and water, the chloroform evaporated, the residue washed with 7 ml. of ether in two portions, and the red crystals of III recrystallized from glacial acetic acid; m.p. 311–312°, mixed with a sample from the Cosgrove–Waters oxidation, m.p. 311–312°, yield 0.4 g.

Reduction of 3,5,3',5'-Tetra-*t*-butylstilbene-4,4'-quinone.—A small amount of the red III was dissolved in 5 ml. of dry butyl ether in a test-tube, a small piece of lithium aluminum hydride added, and the mixture shaken thoroughly. As the color vanished, more of the stilbene quinone was added until about 0.1 g. had been reduced. The solution was diluted with moist ethyl ether, water and dilute hydrochloric acid were added, the mixture shaken, and the organic layer separated. The solvents were removed under vacuum and the pale yellow solid recrystallized three times from dioxane; m.p. 169.5–170°, mixed with IV, m.p. 169.5–170°.

Dealkylation of 3,5,3',5'-Tetra-*t*-butyl-4,4'-dihydroxy-1,2-diphenylethane. A. **By Direct Removal of *t*-Butyl Groups as Isobutylene.**—A solution of 0.3 g. of IV in 20 ml. of purified tetralin was acidified with one drop of sulfuric acid and refluxed 1.5 hours with a slow stream of air sweeping through the apparatus just above the level of condensation of the tetralin vapors. After cooling, the solution was extracted with sodium hydroxide, the phenol precipitated by saturating with carbon dioxide, extracted with ether and the ether evaporated. The oily residue was carefully distilled, yielding a middle fraction (one drop)

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[20] Analyses and molecular weight by H. S. Clark.

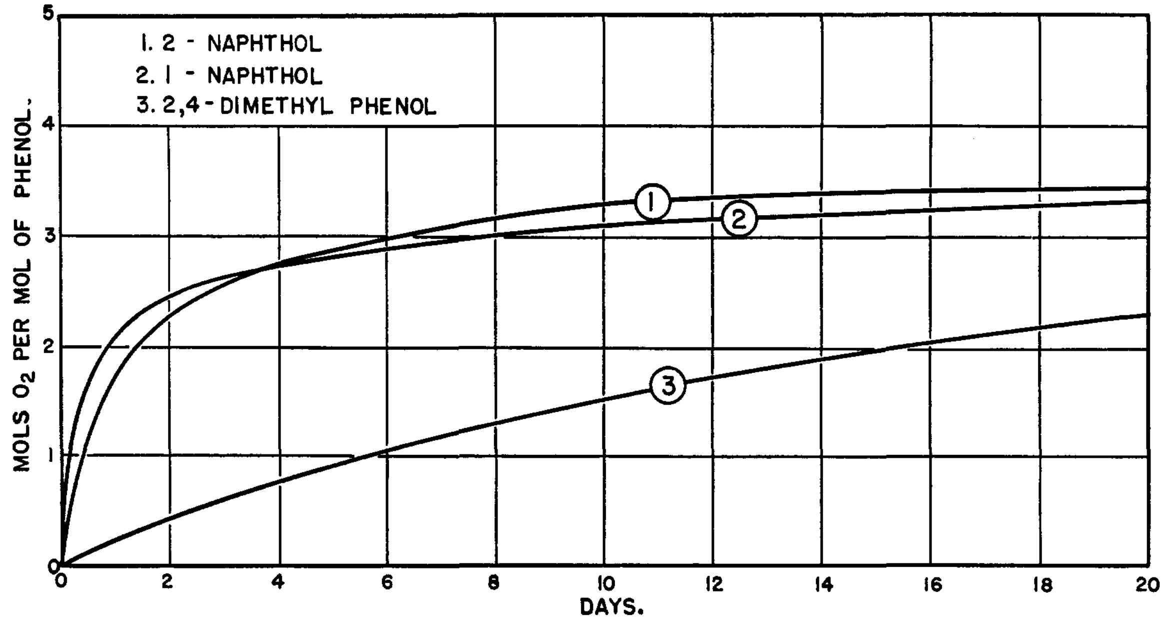

Fig. 2.—Oxidation of disubstituted phenols.

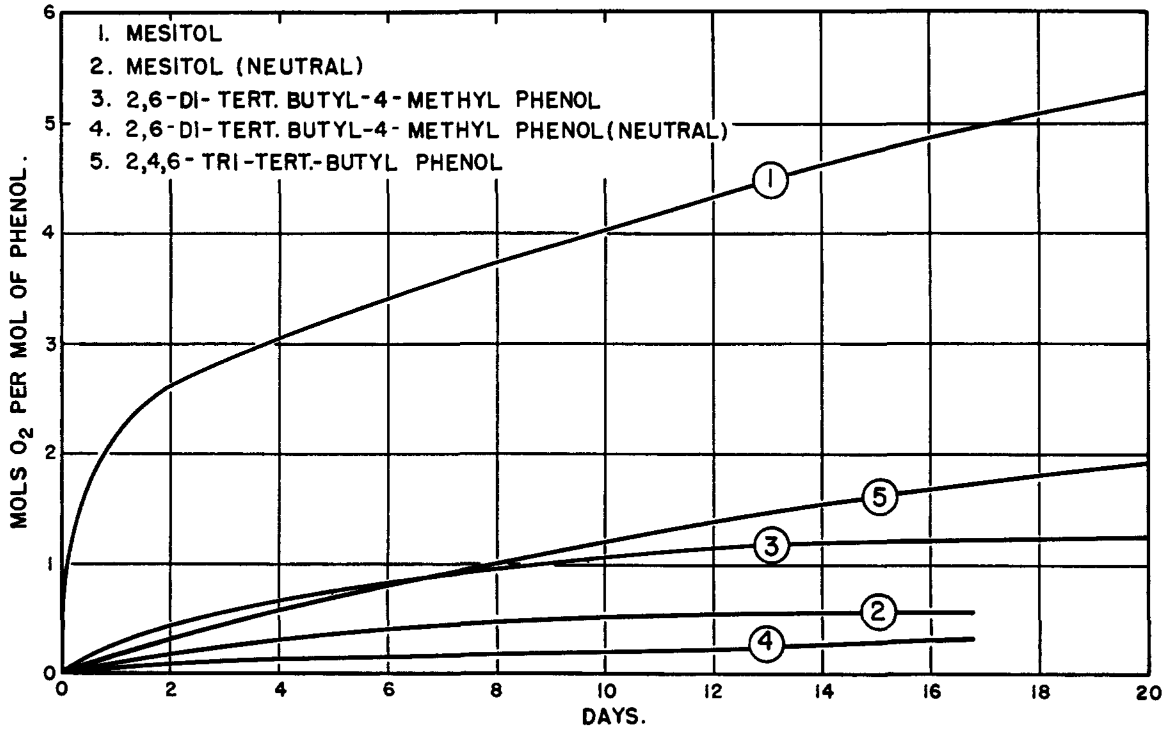

Fig. 3.—Oxidation of trisubstituted phenols.

which solidified. This was recrystallized three times from benzene; m.p. 197–198°. Mixed with an authentic sample of 4,4′-dihydroxy-1,2-diphenylethane, this melted at 197.8–199°. Richardson and Reid[17] reported the melting point of this compound (IV, R = H) as 198–199°.

B. By Transfer of *t*-Butyl Groups to Phenol.—A mixture of 86 g. (0.91 mole) of phenol and 5 g. (0.011 mole) of IV was heated to 50°, three drops of concentrated sulfuric acid added, and the temperature increased to 85° where it was maintained for 24 hours. The mixture was poured into about 800 ml. of water, stirred and filtered. The solid was dissolved in 2 *N* sodium hydroxide, filtered, and the filtrate saturated with carbon dioxide to precipitate IV (R = H); yield 1.3 g. (53% of theoretical), m.p. 197–199°. No attempt was made to isolate by-product *t*-butylphenol.

Synthesis of 4,4′-Dihydroxy-1,2-diphenylethane. A. From 4-Nitrotoluene.—Oxidation of 4-nitrotoluene with air in methyl alcoholic potassium hydroxide[14] gave a 19% yield of 4,4′-dinitro-1,2-diphenylethane, m.p. 180–182°. Reduction of this with tin and hydrochloric acid[15] gave a 92% yield of 4,4′-diamino-1,2-diphenylethane, m.p. 134–135°, which was converted *via* the diazonium reaction[16] to 4,4′-dihydroxy-1,2-diphenylethane, m.p. 196–197°, in 38% yield.

B. From Anisoin.—Anisoin was converted to 4,4′-dimethoxy-1,2-diphenylethane, m.p. 125.5–127°, in 7% yield by Martin's modification of the Clemmensen reduction,[21] and this was hydrolyzed with hydrobromic acid–acetic

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[21] E. L. Martin, THIS JOURNAL, 58, 1438 (1936).

acid[17] to give a 4% yield of 4,4'-dihydroxy-1,2-diphenylethane, m.p. 198–199°.

Discussion

Oxygen Absorption Rates.—It will be seen in Figs. 1 to 3 that in most cases the initial oxidation rate was fairly rapid. Although most of the oxidations were allowed to run for approximately three weeks, in only a few cases did the oxygen absorption rate approach zero (*cf.* 2,6-di-*t*-butyl-4-methylphenol and the naphthols). The oxidation of 2,4-dimethylphenol was allowed to continue for 47 days, at which time the oxygen absorption had reached 3.2 moles per mole of phenol and was still taking place slowly.

Two experiments (Fig. 3) in which the alkali was omitted from the reaction mixture showed a marked reduction in the rate of oxygen absorption. Other workers employing ethanol and toluene solutions of 2,6-di-*t*-butyl-4-methylphenol at room temperature and atmospheric pressure for 50 hours, and at 65.5° and 110 pounds per square inch gage for 23 hours, respectively, have reported recently that this compound did not absorb a measurable amount of oxygen.[22]

A comparison of the oxygen absorption rate curves for the phenols with those of the portions of high-volatile A and B coals capable of being methylated (Fig. 4; these curves, taken from reference 2, were determined as the differences between the rates of oxygen absorption by the original coals and by the coals after methylation with dimethyl sulfate) shows the resemblance with the curves for 4-*n*-butylphenol and the naphthols, respectively. The writers believe, however, that no conclusion as to the structural units responsible for this resemblance is warranted on the basis of present data. It is interesting to note that with the exception of the 4-*n*-butylphenol and possibly the 3-methylphenol, all the phenols tested showed lower oxygen absorption rates than the structures capable of being methylated in the high-volatile B coal and much lower than those of the A coal.

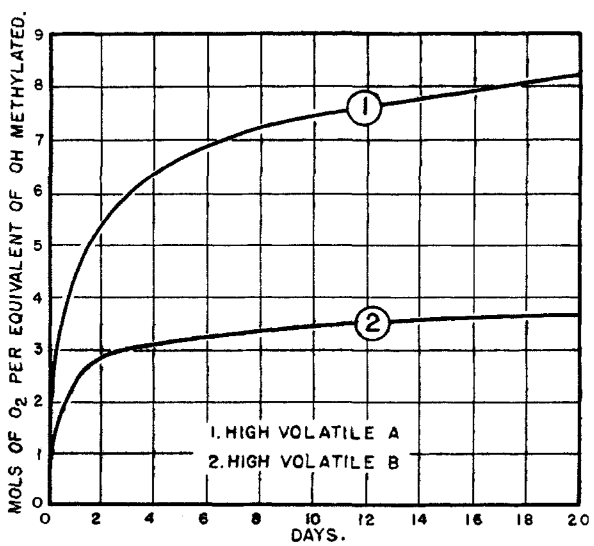
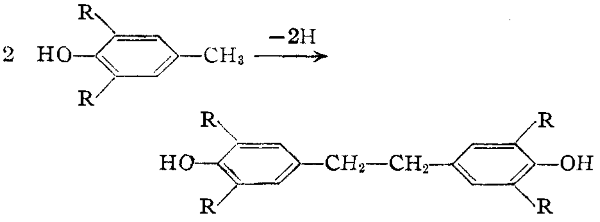


Fig. 4.—Oxidation of bituminous coals.

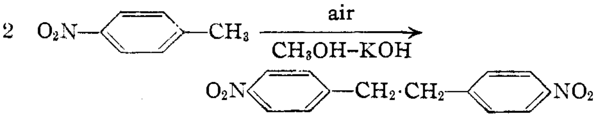
Products of Oxidation.—Although a complete study of the oxidation products was not made, the data of Table I reveal several significant facts. Oxidative degradation, including rupture of the benzene ring, is indicated by the formation of oxalic acid from phenol, the cresols and mesitol; by the formation of carbon dioxide in larger amounts than could be accounted for by side-chain elimination in several cases; and by the production of acetic acid and trimethylacetic acid in several instances.

In the case of 2,6-di-*t*-butyl-4-methylphenol, the neutral oxidation mixture exhibited a red color characteristic of the stilbene quinone III. It seems quite possible that the orange color of the commercial phenol may be due to slight contamination by this oxidation product; this further suggests that this type of oxidative condensation may occur in the absence of alkali and solvent.

Although the conversion of certain 4-alkylphenols to intermediates of the methylene quinone type pictured above may occur under some circumstances, the results of the relatively short time oxidation of 2,6-di-*t*-butyl-4-methylphenol described in the present work, wherein the diphenylethane derivative IV was the predominant alkali-insoluble product and the corresponding stilbene quinone was formed in much smaller quantity indicate that the first stage of the reaction must be a condensation of the type



the diphenylethane derivative being subsequently oxidized to the stilbenequinone. This resembles the alkali-air oxidation of 4-nitrotoluene[14]



It is thus obvious that the chemical changes have not been limited to degradations. The stilbenequinone III and the diphenylethane derivative IV obtained from 2,6-di-*t*-butyl-4-methylphenol are definitely of higher molecular weight than the original phenol, and the properties of the yellow solid from the naphthols and the "humic acids" encountered in a number of the experiments make it appear reasonably certain that they are of greater molecular size than the phenols from which they were made.

"Humic acids," so-called, have been made from a variety of starting materials, some simple molecularly, some complex; they have been made under a variety of conditions, some involving oxidation and others not. In those starting with complex materials, degradative reactions seem to have played the most obvious role, while in other conversions it is apparent that condensation reactions must have played a part.

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(22) M. C. K. Jones, A. R. Jones and B. R. Strickland, *Ind. Eng. Chem.*, **44**, 2721 (1952).

The writers believe that the conversion of coals to "humic acids" by mild oxidation is probably predominantly a degradative change. It is believed, however, that the possibility of the simultaneous occurrence of oxidative condensations must not be overlooked. If the coal contains phenolic structures, or if such structures are formed during the oxidation, it seems possible that such units might undergo a condensation analogous to that described herein while other portions of the coal structure were being converted to simple, water-soluble acids, and acidic groups were being formed from peripheral atoms of the molecules, thus conferring alkali solubility upon the resultant "humic acids." In such a process, much of the nuclear or ring structure of the final product could be that originally existing in the coal, yet some portions of the structure, possibly including quinoid chromophoric groups, might owe their origin to changes taking place during the oxidation. It is therefore believed that an elucidation of "humic acid" structure, while highly desirable from the viewpoint of coal chemistry, would have to be applied with caution to the coal structure problem.

Acknowledgment.—The writers wish to thank William F. Loranger and Elizabeth Bartz Dahlgren, former Research Assistants, for aid in some phases of the laboratory work, and Dr. H. C. Howard of the Coal Research Laboratory of the Carnegie Institute of Technology for very helpful suggestions in the preparation of the manuscript.

URBANA, ILLINOIS

[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER, AND THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Fluorinated Esters. III. Diesters of Carboxylic Acids with Fluorine-containing Alcohols and Glycols[1]

BY ROBERT FILLER, JACK V. FENNER, CHARLES S. STOKES, JOSEPH F. O'BRIEN AND MURRAY HAUPTSCHEIN

RECEIVED NOVEMBER 20, 1952

The preparation of a series of new esters and diesters of carboxylic acids with 1,1-dihydroperfluoro alcohols, a fluorinated secondary alcohol, and an $\alpha,\alpha,\omega,\omega$-tetrahydroperfluoro diol, is described. Physical and chemical properties of these compounds and of several intermediates are presented.

As a continuation of the program correlating various properties with the structure of fluorine-containing esters and diesters,[2,3] this paper describes the preparation and properties of a number of new partially fluorinated diesters. These compounds are mainly derived from dicarboxylic acids and 1,1-dihydroperfluoro alcohols. In addition, a diester obtained from a monocarboxylic acid and an $\alpha,\alpha,\omega,\omega$-tetrahydroperfluoro glycol,[2] has also been prepared. These diesters and several other new, related compounds are listed with their physical properties in Table I.

The 1,1-dihydroperfluoro alcohols and the tetrahydroperfluoro diol were readily prepared by reduction of the corresponding acid chloride or ethyl ester with lithium aluminum hydride.[4,5] The alcohol, $C_7F_{15}CH_2OH$, which has not been described, was prepared by reduction of the corresponding acid chloride, *i.e.*, perfluoroöctanoyl chloride.[2] The secondary alcohol, 4,4,5,5,6,6,6-heptafluoro-3-hexanol, $C_3F_7CHOHC_2H_5$, used to prepare one of the diesters listed in Table I, was obtained as the main product of the reaction of methyl perfluorobutyrate with excess ethylmagnesium halide. A lesser amount of the expected tertiary alcohol, $C_3F_7C(OH)(C_2H_5)_2$, was also isolated.[6]

It was found that the esterification of hydrocarbon dicarboxylic acids with 1,1-dihydroperfluorobutanol in the presence of acid catalysts did not proceed at a practical rate. This was in contrast with the known ease of formation of diesters of perfluorinated acids with unfluorinated alcohols and glycols,[3] but was consistent with our findings in the case of diesters of the type $C_3F_7CH_2O_2C(CF_2)_xCO_2CH_2C_3F_7$.

However, the reaction of dicarboxylic acid chlorides with 1,1-dihydroperfluoro alcohols readily afforded 51–77% conversions to the desired diesters. Similarly, the diester formed from 4,4,5,5,6,6,6-heptafluoro-3-hexanol and adipyl chloride, was readily obtained in 73% yield without any side reactions, due to the great resistance of such fluorine-containing secondary alcohols to dehydration.[7]

While it was desirable to employ acid chlorides for the preparation of diesters of these fluoro alcohols, the diester arising from 1,1,6,6-tetrahydro-1,6-perfluorohexanediol and *n*-butyric acid, could be prepared either directly from the acid using an acid catalyst or from the acid chloride, both methods giving satisfactory yields. However, this fluorinated diol reacted with an excess of a mixture of *n*-butyric anhydride and *n*-butyric acid to give not only the diester but, somewhat unexpectedly, the glycol half-ester, $C_3H_7CO_2CH_2(CF_2)_4CH_2OH$, as

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(1) Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

(2) M. Hauptschein, J. F. O'Brien, C. S. Stokes and R. Filler, THIS JOURNAL, **75**, 87 (1953).

(3) R. Filler, J. F. O'Brien, J. V. Fenner and M. Hauptschein, *ibid.*, **75**, 966 (1953).

(4) A. L. Henne, R. M. Alm and M. Smook, *ibid.*, **70**, 1968 (1948).

(5) E. T. McBee, W. F. Marzluff and O. R. Pierce, *ibid.*, **74**, 444 (1952).

(6) The procedure for the preparation of these alcohols was obtained from a private communication with Dr. O. R. Pierce, Purdue University.

(7) F. Swarts, *Bull. soc. chim. Belg.*, **36**, 191 (1927).