[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY,
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Hindered Diphenoquinones: Diradicals of Oxygen[1]

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Attempts were made to prepare a diphenoquinone having substituents in 2,2'- positions in order to prevent the planarity of the molecule and get a diradical of oxygen. The 2,2'-dimethyl-5,5'-di-t-butyldiphenoquinone was prepared and was shown to be in equilibrium with a small amount of diradical. This compound slowly polymerizes.

It seems clear that the two rings of the diphenoquinone (I) are coplanar, the existence of the central double bond being responsible for this coplanarity. If this coplanarity is destroyed, the central double bond cannot exist and a diradical of oxygen might be expected. The coplanarity of the two benzene rings can be destroyed if one introduces in the 2,2'- positions any substituent which, by steric hindrance, obliges the rings to rotate from a common plane, thus allowing only the existence of a single bond between them.
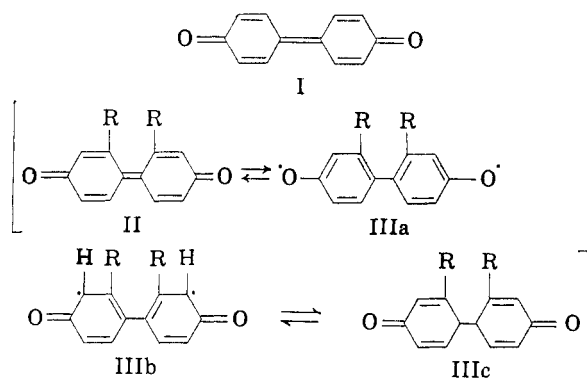
The diradical III would be stabilized by resonance of the different limit forms IIIa, IIIb. In fact, such structures exist: the p,p'-diradical derived from Tchitchibabin's molecule in which are introduced in the 2,2',6,6'- positions substituents

such as methyl or chlorine, IV and V. These compounds isolated in the solid state by Theilacker[3] and Muller,[4] respectively, seem to be examples of diradicals resulting from noncoplanarity of the diphenyl skeleton. These products, almost colorless in the solid state, are deeply colored in solution (red, blue, or green).
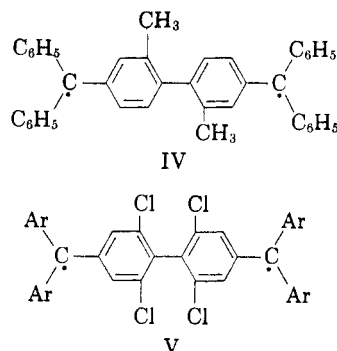
The existence of free radicals of oxygen has been definitely established in the mechanism of oxidation of phenols. The radicals VI, VII, VIII, IX,[5] and X have been proposed as intermediates in the oxidation of the corresponding phenols. The oxidation usually gives a dimer as the final product, for instance XI or XI'.[6]

Some of these free radicals (VII, VIII, IX, for

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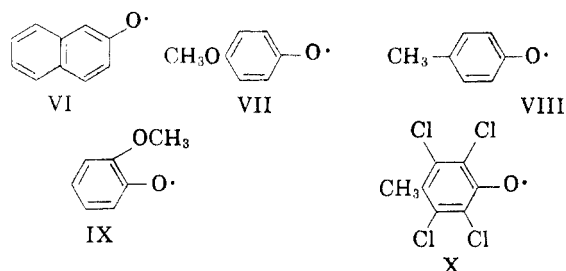
(3) W. Theilacker and W. Ozegowski, Ber., 73, 33, 898 (1940).

(4) E. Muller and H. Neuhoff, Ber., 72B, 2063 (1939); 74, 807 (1941).

(5) S. Goldschmidt, Ber., 55, 3194 (1922).

(6) R. Pummerer, G. Schmidutz, and H. Seifert, Ber., 85, 535 (1952).

VI   VII   VIII

IX

X

example) made their appearance as a fugitive coloration during the reaction. Others exist in solution in a state of equilibrium with the dimer, for example the phenanthryl XII (R = OEt, Cl...) which exists in the solid state as a dimer XIII, dissociates partially in solution into a free radical (green).[5]

XI

XI'

XII   XIII
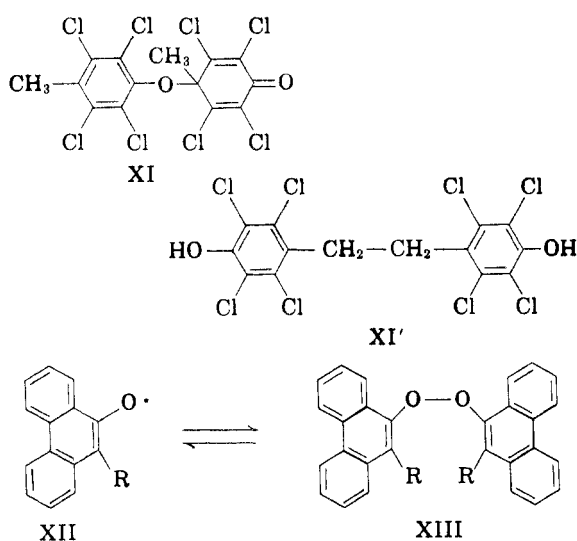
And recently, Muller[7] isolated a free radical of oxygen in the solid state. The tri-t-butylphenoxy (XVI) was obtained by oxidation of the corresponding phenol or by removal by silver of a halogen (chlorine or bromine) from the halogenated compound XV.
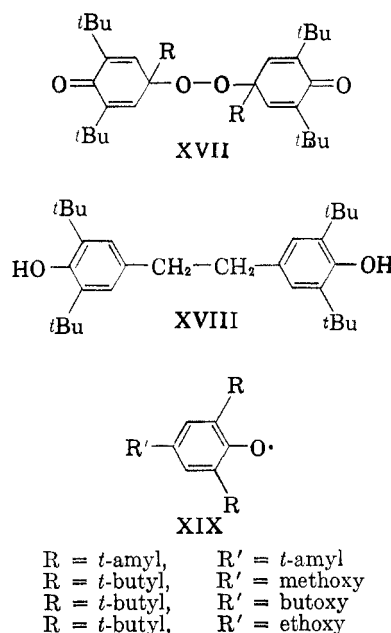
Muller explained the relative stability of this

XIV   XV

XVI

a   b

c
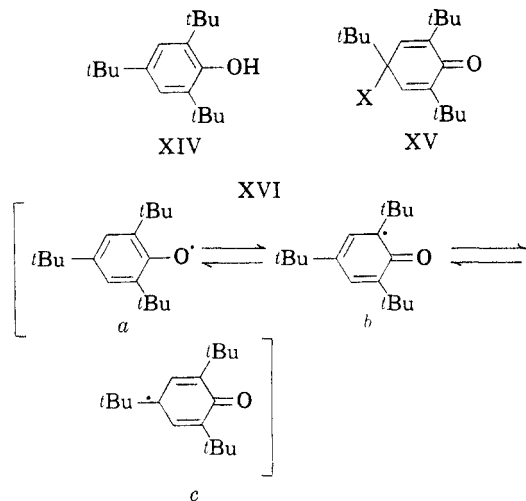
(7) E. Muller and coworkers, Ber., 87, 922, 1605 (1954).

free radical by the steric hindrance introduced by the t-butyl groups which prevents the approach of reagents to the molecule. This free radical, deeply blue in the solid state, decolorized rapidly in the presence of air by formation of peroxide XVII.

In the same way, Cook[8] prepared similar stable free radicals (XIX) and showed that these free radicals could exist when the o- and p- positions were substituted to prevent dimerization and when there was no hydrogen on the α-carbon. Thus, with α-hydrogen present, the 2,6-di-t-butyl-4-methyl-phenoxy gives the dimer XVIII.

XVII

XVIII

XIX

R = t-amyl,   R' = t-amyl
R = t-butyl,   R' = methoxy
R = t-butyl,   R' = butoxy
R = t-butyl,   R' = ethoxy

All these facts encouraged the assumption that it should be possible to obtain a diradical such as III. As a matter of fact, the dianthrone XXa, which gives a yellow solution at room temperature, gives green solutions when heated to 265°. Some authors[9] explained this fact by the existence of the diradical form b, and LCAO-MO calculation[10] suggests that bianthrone would exist in a triplet state by rotation of one of the anthracene rings. On the other hand, some other compounds (XXI, XXII, XXIII, XXIV, XXV)[11] derived from 2,2'-disub-

(8) C. D. Cook and coworkers, J. Org. Chem., 18, 261 (1953); J. Am. Chem. Soc., 75, 6242 (1953); J. Am. Chem. Soc., 77, 1783 (1955); J. Am. Chem. Soc., 78, 2002 (1956).

(9) W. T. Grubb and G. B. Kistiakowsky, J. Am. Chem. Soc., 72, 419 (1950); W. G. Nielsen and G. K. Fraenkel, J. Chem. Phys., 21, 1619 (1953); W. Theilacker, G. Kortum, and G. Friedheim, Ber., 83, 508 (1950).

(10) Matlow, J. Chem. Phys., 23, 152 (1955).

(11) N. A. Valyashko and M. M. Scherbak, J. Gen. Chem. U.S.S.R., 8, 1597 (1938); XXI: F. Henrich, Ber., 71B, 2049 (1938) [Chem. Abstr., 33, 165 (1939)]; F. Henrich, Sitzber. physik. med. Sozietät Erlangen, 71, 199 (1939) XXII: C. V. Bordeianu, Ann. sci. univ. Jassy, I, 23, 240 (1937) [Chem. Abstr., 32, 5802 (1938)]. XXIII: G. Sanna and T. Zucca, Rend. seminar. Fac. sci. univ. Cagliari, 19, 155 (1949) [Chem. Abstr., 46, 7087 (1952)]. XXIV: A. A. Levine, J. Am. Chem. Soc., 48, 797, 2719 (1926). XXV: F. D. Smith, U.S. Patent 2,449,088, Sept. 14, 1948 [Chem. Abstr., 43, 813c (1949)].

stituted diphenoquinone are claimed to have been obtained and are described as having a quinoid structure, but no real proofs of structure were given and no studies on the properties of these products have been reported.

a   XX   b

XXI

R = CH₃ or — CH⟨CH₃ CH₃

XXII

XXIII

XXIV
X = Br or Cl

XXV
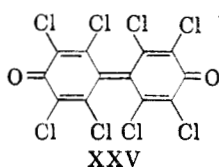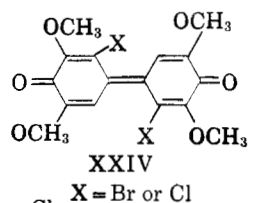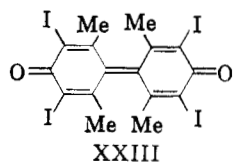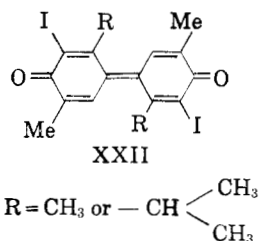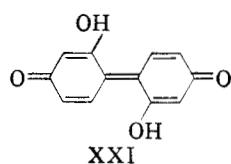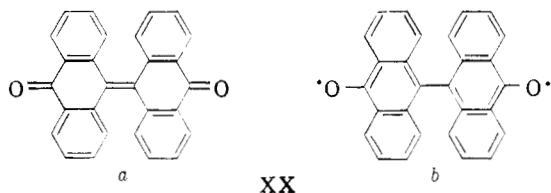
So we proceeded to the synthesis of a biphenol, 2,2′,6,6′-tetrasubstituted, without ambiguity in its constitution and potentially able to give by oxidation the expected diradical of oxygen.
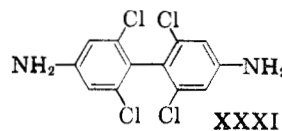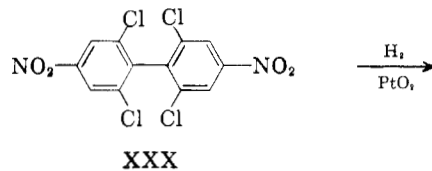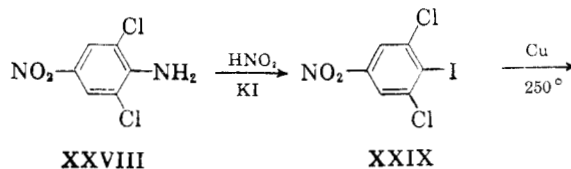
Polychlorobiphenols and their oxidation. The diradical whose preparation was first attempted was the tetrachloro 2,2′,6,6′-diphenoxy XXVIIa which ought to result from the oxidation of the corresponding biphenol XXVI.


XXVI

XXVII
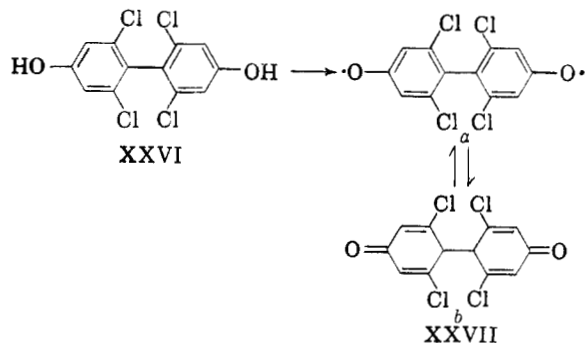
The method chosen for the synthesis of the biphenol is the following:

XXVIII   XXIX

XXX

XXXI   Biphenol

The compounds XXIX, XXX, and XXXI had been prepared by other authors using different methods, but the process used here gave better yields and the products obtained were much easier to purify than those obtained by the previous methods.

The structure of the biphenol was further confirmed by its spectrum (Fig. 1), similar to the spectrum of the pentachlorophenol and differing from the one of biphenol and 3,3′-dimethylbiphenol. The usual oxidizing agents were tried without success, the biphenol remaining unchanged. (Silver oxide[12] or lead dioxide in anhydrous ether or benzene, lead dioxide in moist ether,[5] ferric chloride in acetic acid, potassium permanganate in alkaline solution.) Potassium permanganate in acid solution completely destroyed the molecule, as was shown by U.V. examination.

Then the action of chlorine was tried, expecting the formation of the octachlorobiphenol XXXII which, by further oxidation, might give the diradical XXXV. Chlorine in chloroform gave the expected octachlorobiphenol XXXII.

XXXII   XXXIII

XXXIV   XXXV
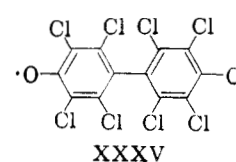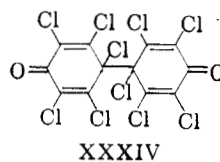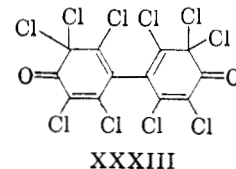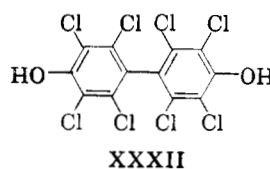
The structure of octachlorobiphenol XXXII was confirmed by its U.V. spectrum (Fig. 1), similar to the spectrum of the pentachlorophenol. Chlorination of either tetrachloro- or octachlorobiphenol in acetic acid solution gave a decachlorinated com-

(12) R. Willstätter and F. Müller, *Ber.*, **41**, 2580 (1908).
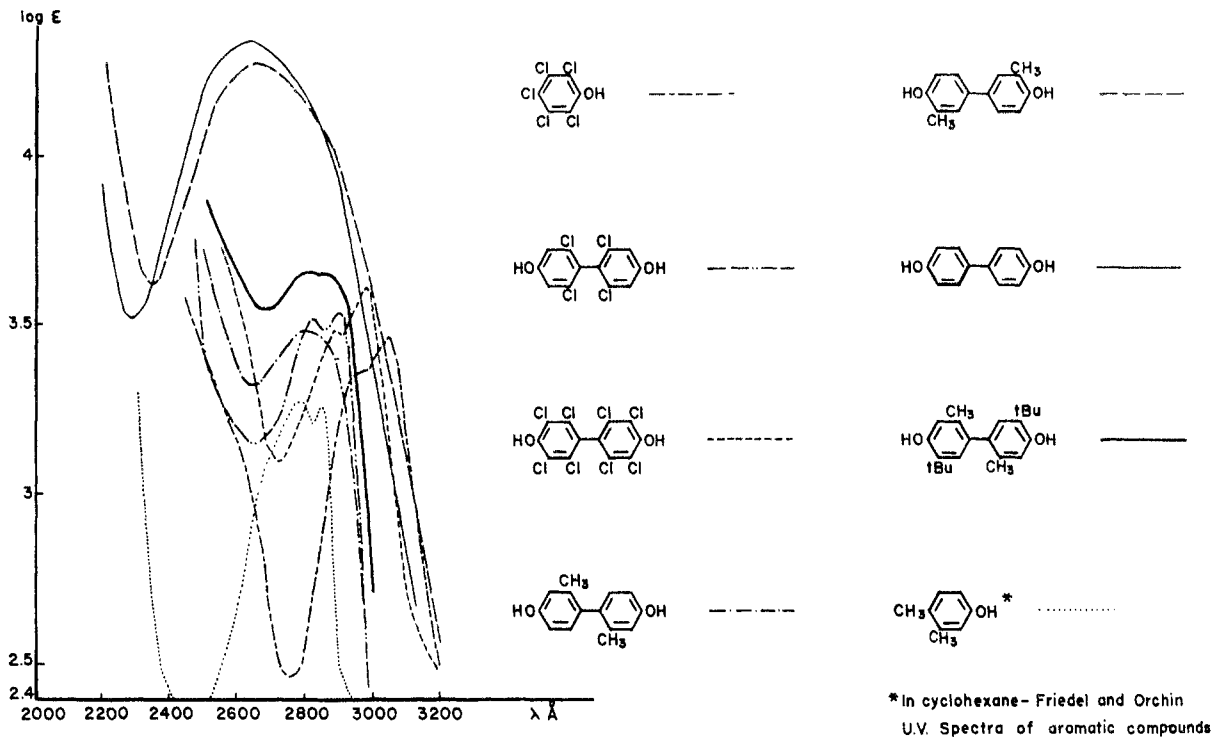
Fig. 1.—U.V. Spectra in Alcohol

pound for which two structures were possible: XXXIII and XXXIV. Reaction with zinc and acid gave the octachlorobiphenol, showing that the diphenyl skeleton had been preserved.

An o-quinoid structure (XXXIII) was suggested by the U.V. spectrum (Fig. 2). The spectrum of the decachloro- compound is very similar to the spectrum of o-benzoquinone and quite different from the spectra of hexachlorophenol XXXVII and p-benzoquinone. In fact, the o-quinoid structure is more probable for steric reasons than the p-quinoid structure XXXIV.
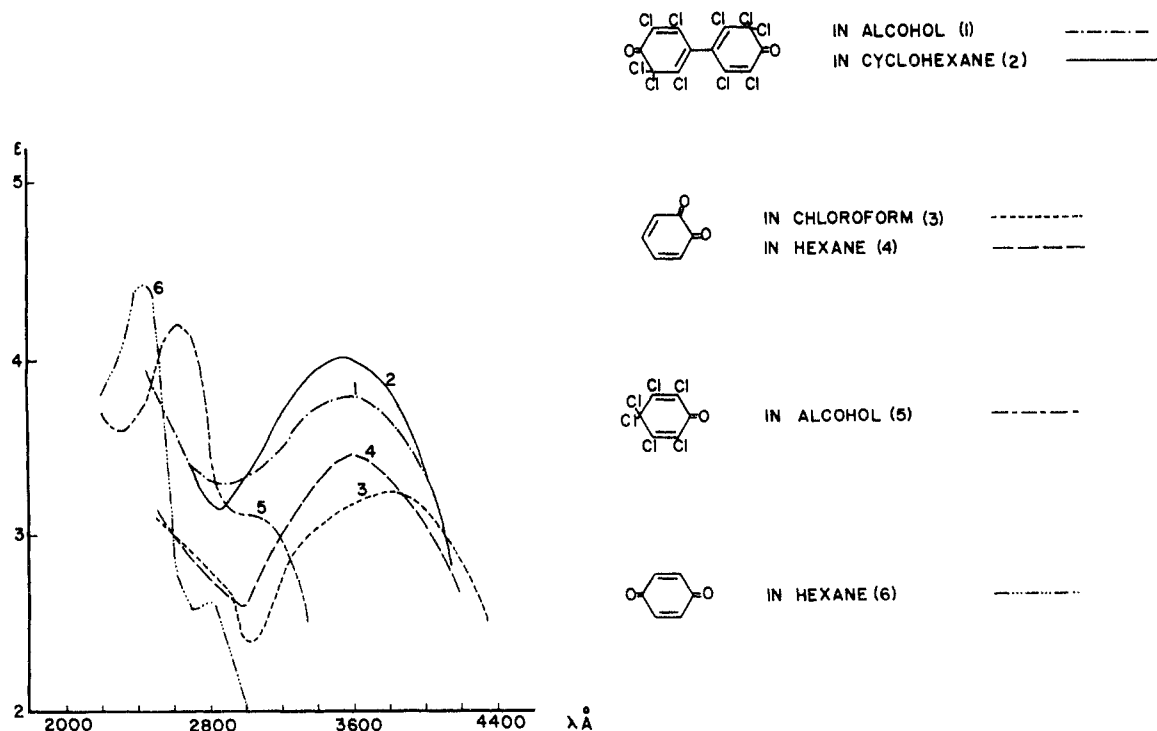
Fig. 2.—U.V. Spectra of Decachloro Compound and Analogs.   [See Friedel and Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, p. 77; Goldschmidt, *Ber.* **61**, 1868 (1928)]
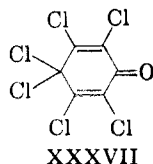
XXXVII

It should be noted that the decachloro compound XXXIII is slowly reduced to octachlorobiphenol by alcohol at room temperature (complete reaction in approximately 24 hr.), showing the same behavior as the hexachlorophenol XXXVII toward this solvent. This reduction is approximately ten times faster with the diphenyl compound.

The 2,2′,3,3′,5,5′,6,6′-octachlorobiphenol seems even less sensitive toward oxidizing agents than the tetrachloro-compound.

None of the following reagents gave any color to the solution; that is to say, no formation of a radical: lead dioxide in moist ether or in benzene, alkaline potassium ferricyanide in benzene under nitrogen, potassium dichromate in boiling acetic acid with traces of sulfuric acid, potassium permanganate with sulfuric acid. In most cases, the biphenol was left unchanged. The action of aqua regia for one month at room temperature according to the method used by Smith,[11] reported to prepare the same product, was here completely unsuccessful; the starting material was recovered unchanged.
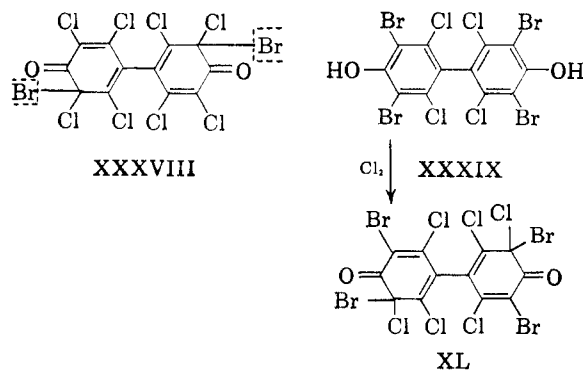
Thus, neither the diradical XXXV nor the diphenoquinone XXV could be obtained because of the strong resistance of this biphenol toward the oxidizing agents.

After these failures, another completely different method was tried. This method consisted in the removal of two extra atoms of chlorine from the decachloro-compound XXXIII by the action of silver in benzene solution. For this procedure we refer to the reaction used by Muller[7] to prepare the tri-t-butyl-phenoxy radical. In this case, however, after 18 hr. of agitation of the solution with active silver under pure nitrogen, the decachloro-compound XXXIII was recovered unchanged.

Since the two chlorine atoms seemed to be too tightly bound to the molecule, we tried to replace them by two bromine atoms, as in XXXVIII. This compound might be expected from bromination of the octachlorobiphenol, but the only prod-

uct obtained by several procedures was a substance with the properties of a polymer. Next we tried bromination of the tetrachlorobiphenol to get XXXIX, followed by chlorination giving XL which possesses the desired chlorine and bromine on the same carbon atom.

The tetrabromo compound XXXIX was obtained by action of bromine on tetrachlorobiphenol. Then the chlorine was allowed to react in MeOH-AcOH[7] and even at −20° the bromine was replaced by the chlorine with production of the decachloro compound XXXIII previously described.

From all the foregoing observations the idea arises that perhaps the presence of the electronegative chlorine prevents the oxidation of the biphenol and the formation of the diradical.

A test of this notion was made by a study of pentachlorophenol and attempts to prepare the corresponding radical (XLI).

Most of the strong oxidizing agents[13] transform pentachlorophenol into chloranil by removal of p-chlorine. An analogous reaction is observed with sym-trichlorophenol.[14] Such results could not be expected for the octachlorobiphenol.

XLI
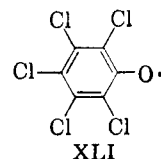
The lead dioxide in moist ether at 0° gave no color and neither did potassium ferricyanide in alkaline solution, differing in this way from tri-t-butylphenol. Pummerer reports that the dehydro-tetrachloro-p-cresol, X-XI, a strong oxidizing agent, was without action on pentachlorophenol.[6]

2,2′-Dimethyl-p,p′-biphenol and its oxidation. So we tried to prepare a diradical free from chlorine and for this purpose the 2,2′-dimethyl-p-biphenol XLII was prepared. The angle between the two phenyl rings ought to be smaller than with four chlorine atoms and it may be expected that some stabilization of the diradical XLIII by the methyl groups should be apparent.

XLII   **XLIII**

XLIV
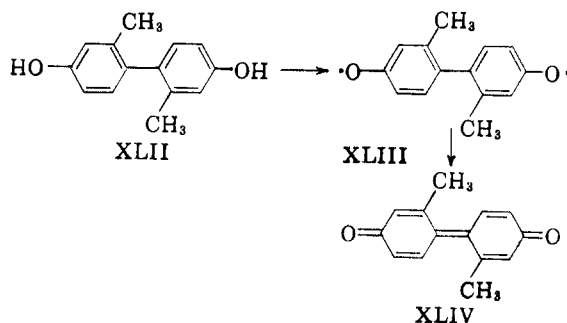
The 2,2′-dimethylbiphenol was prepared in the following way:

(13) Beilstein, **VI**, 194.
(14) W. H. Hunter and M. Morse, *J. Am. Chem. Soc.*, **48**, 1615 (1926).

XXXVIII   **XXXIX**

XL

XLV → XLVI → biphenol XLII
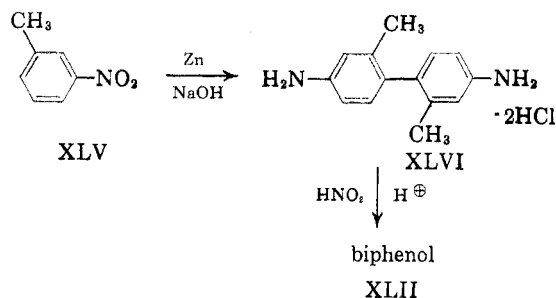
The alkaline reduction of *m*-nitrotoluene by zinc and alcohol gives, directly after acidification, a very good yield of the diamine which is transformed into biphenol in the usual way.

The diamine XLVI has been prepared in another way:

XLVII → XLVIII → diamine hydrochloride XLVI
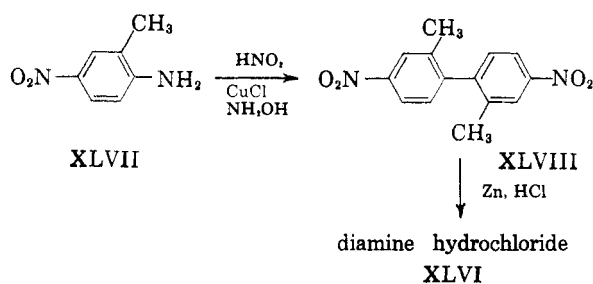
In contrast with the other biphenols, an easy oxidation was possible, although it was not possible to see any color of a diradical. An insoluble brown polymer was formed by action of potassium ferricyanide. This polymer was mostly absorbed by lead dioxide when using this reagent. The same result was observed even at low temperature (−80°) under pure nitrogen.

From these facts we were led to believe that the biphenol XLII was oxidized, presumably with formation of the diradical, but that this reacted further to give dimers or polymers.

2,2'-Dimethyl-5,5'-di-t-butylbiphenol and its oxidation. As suggested by Muller,[7] two *t*-butyl groups in positions ortho to the hydroxyl increase the stability of the corresponding free radical by steric hindrance, in preventing the approach of the reagents to the molecule.

So, in order to stabilize the diradical (XLIII) we tried to introduce four *t*-butyl groups in the 3,5,3',5'-positions of the 2,2'-dimethylbiphenol (XLII). According to the method of alkylation of phenol,[15] isobutylene was allowed to react with the dimethylbiphenol at 70° in benzene solution with a trace of sulfuric acid. Under these conditions, only two *t*-butyl groups could be introduced in the 5,5'-positions apparently because of the hindrance of the two methyl groups preventing the substitution on the 3,3'-positions.[16]

(15) G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Am. Chem. Soc.*, **67**, 303 (1945).

(16) M. J. Schlatter and R. D. Clark, *J. Am. Chem. Soc.*, **75**, 361 (1953); E. E. Burgoyne, T. E. Close, and D. K. Watson, *J. Org. Chem.*, **20**, 1508 (1955).

The 2,2'-dimethyl-5,5'-di-*t*-butylbiphenol, in accordance with the observation by Stillson[15] for similar hindered phenols, is not soluble in dilute alkali and could be purified from other phenols by use of this property. Its spectrum (Fig. 1) is similar to the spectrum of the 2,2'-dimethylbiphenol, showing that the two benzene rings are not coplanar.

XLIX → L → LI
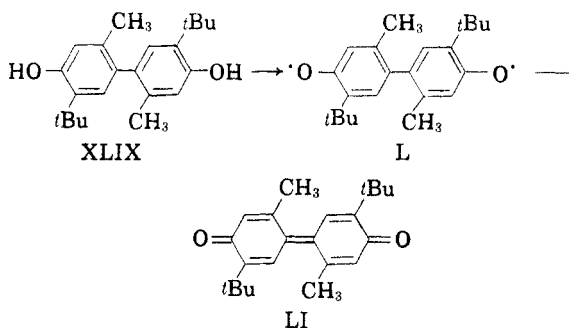
In contrast to the other biphenols prepared above, this one gives deeply colored solutions with oxidizing agents. Thus, with lead dioxide in moist ether or in benzene, we readily got a deep red solution stable several hours. The same result was obtained with alkaline potassium ferricyanide.

According to our hypothesis, these solutions could contain the diradical (L) or the quinone (LI) or a mixture of the two products in equilibrium L ⇌ LI, and/or products of polymerization.

In fact, studies of electronic paramagnetic spin resonance (ESR)[17] and optical spectra of these solu-
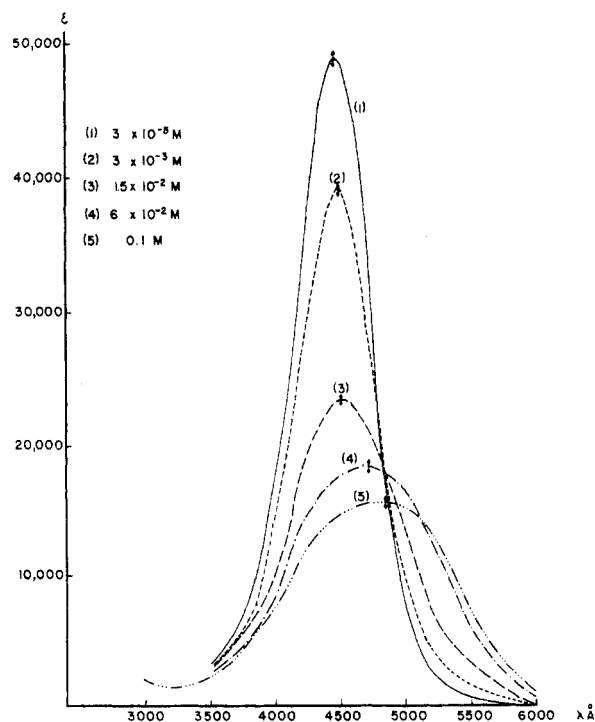
FIG. 3.—SPECTRA OBTAINED BY OXIDATION WITH LEAD DIOXIDE UNDER VACUUM AT DIFFERENT CONCENTRATIONS OF BIPHENOL IN BENZENE

(17) J. E. Werz. *Chem. Revs.*, **55**, 830 (1955).

tions showed that the reaction of oxidation was a complex phenomenon involving several steps. Most of this study was done in benzene solution with lead dioxide as oxidizing agent. The solutions obtained were somewhat more stable when free from oxygen; therefore, many experiments were carried out under nitrogen or under vacuum.

A solution of biphenol in benzene was shaken with lead dioxide until the reaction was complete. This was indicated when the principal absorption band of the spectrum reached an apparent maximum (about 15 min.). Results, shown in Fig. 3, demonstrate that the reaction follows a different course when it is done in dilute or in concentrated solution.

In dilute solutions $(3 \times 10^{-5}$ mol./l.) the absorption spectrum of the reaction product exhibits
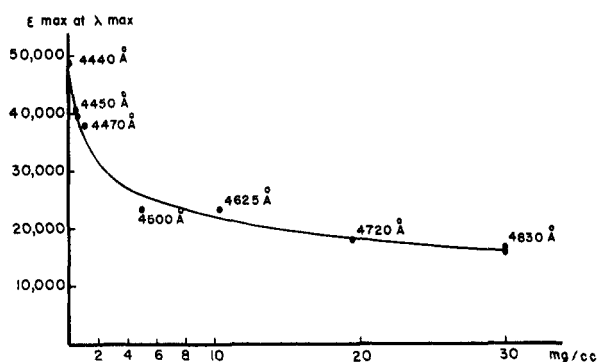
FIG. 4.—APPARENT ϵ_{max} AS A FUNCTION OF CONCENTRATION OF THE REACTION; VALUES CORRESPONDING TO CURVES OF FIG. 3.

one band (Fig. 3: $\lambda_{max} = 4440$ Å, ϵ_{max} approximately 49,000), indicating that there is only one compound in the solution which is, as it will be shown later, the hindered diphenoquinone LI. When the concentration of the solution is increased (Figs. 3 and 4), λ_{max} of this band is shifted toward the longer wave length (4830 Å) and ϵ_{max} decreases considerably and settles for a saturated solution of the starting diphenol to a value of 16,000 (Fig. 4). A new maximum becomes apparent at 5000 Å producing a broadening of the entire absorption (Curve 5, Fig. 3). It is apparent that a polymerization of the hindered quinone LI occurred with the increase of the concentration.

This study will, therefore, be divided into two parts: (1) study of the hindered diphenoquinone (produced in dilute solution), and (2) study of the polymerization products (in concentrated solution).

(*1*) *Hindered diphenoquinone* (*dilute solutions*). Several lines of evidence were used in establishing the structure of this compound.

In Fig. 5 optical spectra of this quinone LI, diphenoquinone I, 3,3′-dimethyldiphenoquinone, Tchitchibabin's hydrocarbon and hindered Tchitchibabin's hydrocarbon IV are compared. From the behavior of the spectra we can be confident that dilute solutions $(3 \times 10^{-5}M)$ contain almost exclusively the quinone LI.

Such a hindered diphenoquinone should have a higher oxidation potential than diphenoquinone itself. This was established by the reaction of biphenol with the hindered quinone:
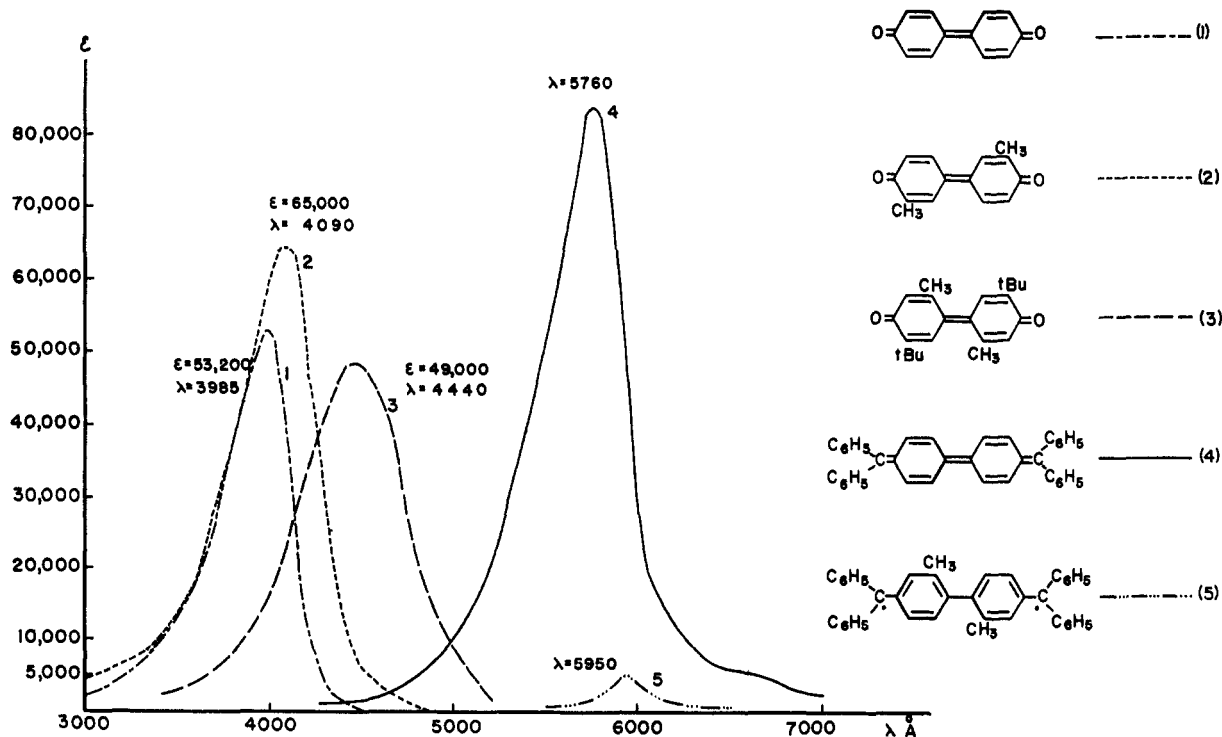
FIG. 5.—SPECTRA IN BENZENE OF HINDERED DIPHENOQUINONE AND ANALOGS
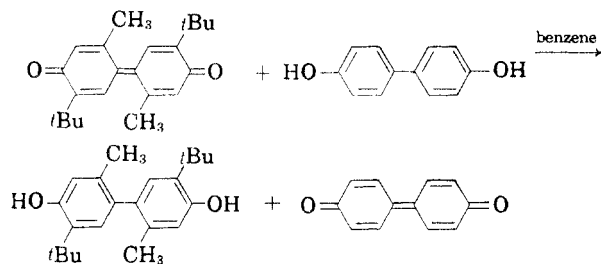
The exchange between the two compounds takes place in a few hours in benzene-ether solution with production (according to the spectrum, Fig. 6a)

itself or with biphenol XLIX, giving dimers LIII and trimers LV, LVII with a quinoid structure. Several facts support this suggestion:

(a) The 390 Å shift of the absorption band toward the red and the decrease by two thirds of the corresponding ϵ_{max} value from their value in the dilute solution.

(b) The titration of oxidation equivalents by sodium iodide and thiosulfate gave a value of 0.24 to 0.52 per molecule of starting biphenol. The diphenoquinone LI would give 2 equivalents per molecule and the trimer LIV should give 0.66.

Fig. 6

(a)   Action of biphenol (3 mol.) on the hindered diphenoquinone (1 mol.) in benzene. Quinone prepared in dilute solution.

(b)   Action of biphenol (7 mol.) on the so-called trimer quinone (1 mol. monomeric unit) in benzene. Trimer prepared in concentrated solution.

of 0.86 molecule of diphenoquinone per molecule of oxidized hindered biphenol (or 0.95 per molecule of apparent hindered quinone formed).

The hindered diphenoquinone LI, according to our hypothesis, is supposed to be in equilibrium (LI ⇌ L) with the diradical L. This radical could be observed directly only in a more concentrated solution (10^{-3} mol./l., Curve 2, Fig. 3. ϵ_{max} = 39,600) by ESR studies. A weak signal (G = 2) was obtained corresponding to a content of about 1 free electron for 1000 to 2000 molecules.

(2) *Polymerization products (concentrated solutions).* We have mentioned above the possibility of a polymerization in concentrated solutions. The molecule of diphenoquinone LI is able to react with

(c) The products of the iodide reduction are weakly colored, possess a spectrum very similar to the starting biphenol, have a very low solubility, and cannot be sublimed, thus differing from starting biphenol.

(d) The action of biphenol in benzene, as above for the diphenoquinone LI, gave a similar result (Fig. 6b), that is to say, reduction of the quinoid polymers with simultaneous formation of diphenoquinone. The reaction established the diphenoquinoid structure of these polymeric compounds; 0.32 to 0.53 molecules of diphenoquinone were formed per molecule of starting hindered biphenol (0.64 to 1.06 oxidation equivalent).

The discrepancy between these values and the

one found in experiment (b) can be explained by the presence of varying amounts of peroxides due to varying conditions in the two experiments.

(e) The successive polymerization reactions which occur during the oxidation of the hindered biphenol could be realized in several separated

```
- - - - - - - -   Decay of the hindered monomeric dipheno-
                    quinone (LI)
————————         Action of 1 mol. of hindered biphenol on 1 mol.
                    of hindered biphenoquinone
—·——·——·—       Decay of the so called dimer diphenoquinone
                    (LIII)
—·——·——·—       Action of 1 mol. of hindered biphenol on 1 mol.
                    of dimer diphenoquinone
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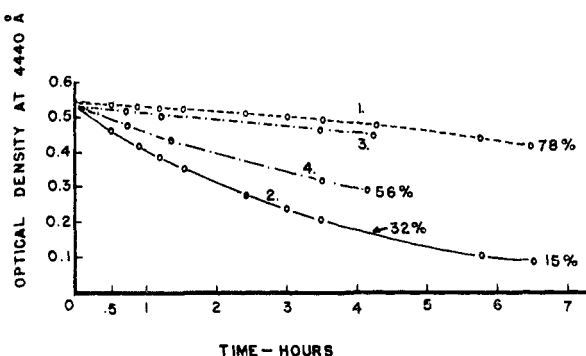

FIG. 7.—OPTICAL DENSITY AT λ = 4440 Å AS A FUNCTION OF TIME IN BENZENE AT ROOM TEMPERATURE

steps with production of some of the hypothesized intermediate compounds (Figs. 7, 8, and 9).

To a dilute solution of monomeric quinone LI (λ_{max} 4440, Σ_{max} 44,000, Curve 1, Fig. 8) was added a solution of hindered biphenol (1 mol. for 1 mol.). The solution was slowly decolorized at room temperature and after 6.30 hr. (Curve 2, Fig. 7) 85% of the quinone had disappeared. (The reaction could be accelerated by heating at 50–70°.) At the same time, a solution of quinone LI alone (at the same total molar concentration) decayed by only 22% (Curve 1, Fig. 7).

The resulting decolorized solution, supposed to contain the dimer LII, (Fig. 9) was shaken 2 min. with lead dioxide, resulting in formation of an orange solution (λ_{max} 4470, ϵ_{max} = 25,000, Curve 2, Fig. 8), corresponding to the dimer quinone LIII.

Then to this solution was added, once more, the hindered biphenol (1 mol. for 1 mol. of dimer), resulting in the fading of the solution. The reaction was slower (Curve 4, Fig. 7) than the first one (about one half) due to the hindrance of one of the functions of the diphenoquinone in the compound LIII.

Then this solution, supposed to contain the trimer LIV, was shaken 2 min. with lead dioxide and gave
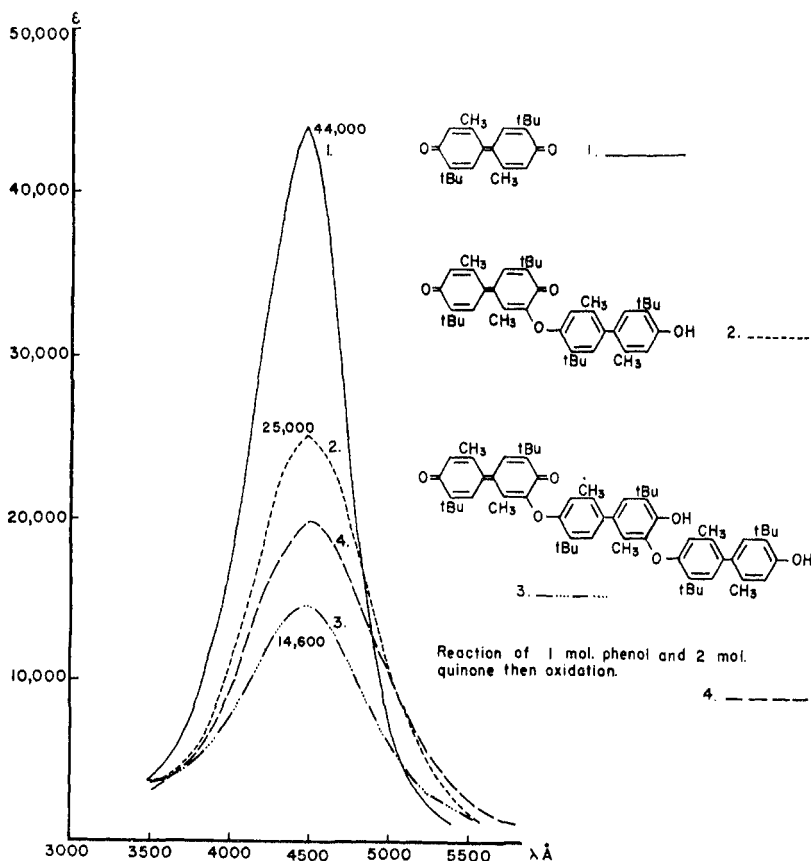
FIG. 8.—SPECTRA IN BENZENE OF THE HINDERED QUINONES, CALCULATED WITH M = 326
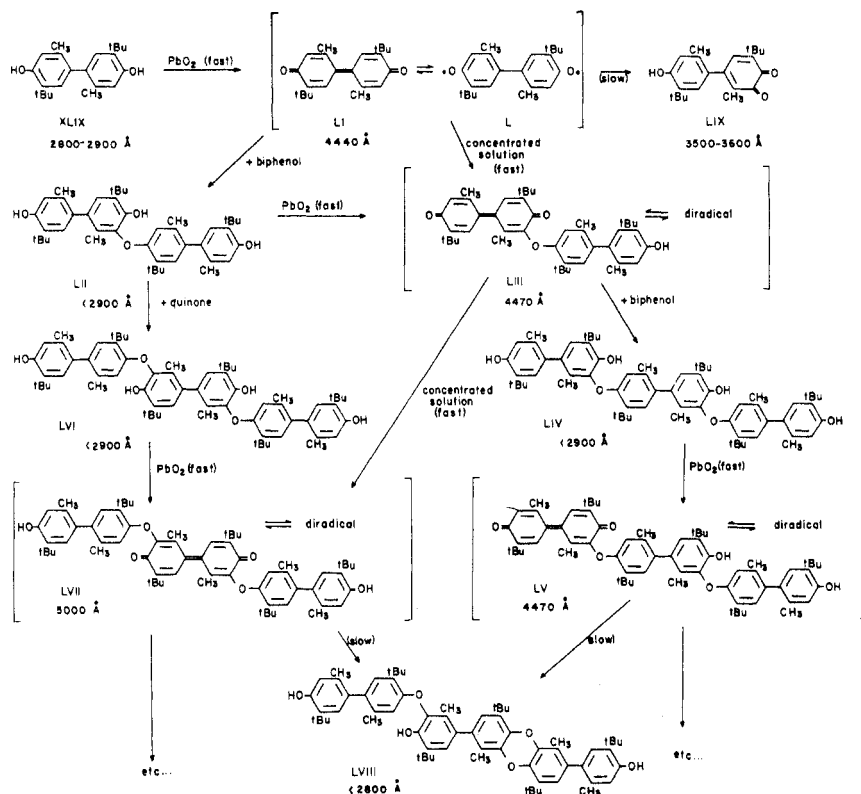
FIG. 9.—OXIDATION OF HINDERED PHENOL

an orange solution (λ_{max} 4470, ϵ_{max} = 14,600, Curve 3, Fig. 8). The three successive values of ϵ_{max} (44,000, 25,000 and 14,600) are in fairly good agreement with the formation of the monomer LI, dimer LIII, and trimer LV quinones.

The absorption observed at 5000 Å in very concentrated solutions (Curve 5, Fig. 3) should be attributed to a trimer quinone such as LVII, which can be produced when an excess of quinone LI is present in the solution (Fig. 9, LI → LIII → LVII or LI → LII → LVI → LVII).

This was partially accomplished in dilute solution by allowing 1 molecule of hindered biphenol to react with 2 molecules of quinone LI. After almost complete bleaching of the solution corresponding to the formation of LVI and LIV, the oxidation as above gave an orange solution. This solution (λ_{max} 4500, ϵ_{max} = 19,800, Curve 4, Fig. 8) exhibits a definite increase of absorption at 5000 Å.

Free radical content. The presence of free radicals in solutions containing these quinoid compounds (LIII, LV, LVII) was shown, as for the monomeric quinone, by ESR studies. A signal (G = 2) was found, indicating a content of about 1 free electron for 800 monomeric units, a value somewhat higher than for the monomer. This would correspond to one electron for the approximately 270 molecules of trimer LVII.

Compounds with such a quinoid structure should be in equilibrium with the corresponding diradical and therefore the ESR signal should show a de-

pendency on temperature, that is to say, an increase of diradical content by heating and a decrease in cooling (Nielsen and Fraenkel).[9] Such a reversible increase of ESR signal between 30° and 100° was found (Fig. 10) until the quinone was completely transformed by polymerization and cyclization (LVIII). This transformation takes place faster than at room temperature.

FIG. 10.—INFLUENCE OF TEMPERATURE ON THE INTENSITY OF THE ESR SIGNAL OF THE HINDERED QUINONE

Unfortunately, such an effect could be studied only on the polymers (LIII, LV, LVII) and not on the quinone (LI) in the very dilute solution, because of the weakness of the signal.

Decay of the compounds (Figs. 11 and 12). According to the ESR signal, the proportion of the free radical is higher in concentrated solution and reaches a val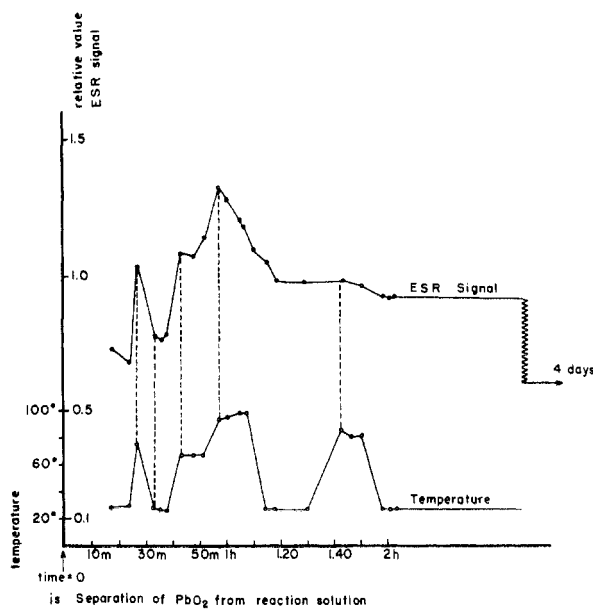ue of about 1 free electron for 600 to 1000 monomeric units (average 800). When the concentrated solution is freshly oxidized, the signal is even higher (1 electron for 200 units), but decays in less than half an hour and drops to the rather stable value of 1 electron for 800. During the

FIG. 11.—DECAY OF THE HINDERED QUINONE IN A CONCENTRATED BENZENE SOLUTION ($^1/_{10}$ MOL./L.) UNDER VACUUM AS A FUNCTION OF TIME (SPECTRA IN BENZENE)

same time the ϵ_{max} of the optical spectrum is decreasing more slowly (Fig. 12). This discrepancy between the behavior as the function of time of the ESR signal and optical absorption would indicate the initial presence of some unstable free radical produced during the reaction (probably a monoradical). After decay, the signal of this radical can be regenerated by addition of lead dioxide.

All these solutions are decolorized after 1 or 2 days. This fading corresponds to the disappearance of the main band (4440–5000 Å, Fig. 11).

The spectra shown in Fig. 13 (Curves 3, 4, and 5) correspond to transformation products from various sources and show the absorption band of phenol (2800 to 2900) and a general increase of absorption below 2800 as compared to the absorption of the quinone (Curve 1) and of the biphenol (Curve 2). Sometimes a peak (Fig. 11 and 13) is found around 3400–3600 Å, which could indicate formation of an orthoquinone LIX by oxidation.

Attempts to isolate quinones as solids. All the above experiments were carried out in solutions. Some attempts were made to prepare a solid sample from 0.01M solution.

One obtains, in all cases, a red glass, giving, in chloroform, a spectrum similar to the one of Curve 5, Fig. 3, corresponding to the structure LVII. This red glass has a somewhat higher content of free radical ($^1/_{100}$, G = 2.0). It decays rapidly in the presence of air, more slowly in vacuum, giving a yellow powder. The ESR signal can still be observed, approximately $^1/_{800}$, in the almost completely transformed material (Curve 3, Fig. 13), indicating the trapping of free electrons in the polymer, which would have a structure derived from LVIII. The analysis of the red glass is in agreement with the theory.

Fig. 9 gives a proposal for the complete scheme of oxidation and polymerization. It is a hypothesis which fits quite satisfactorily all of our various observations. The results demonstrate that as few
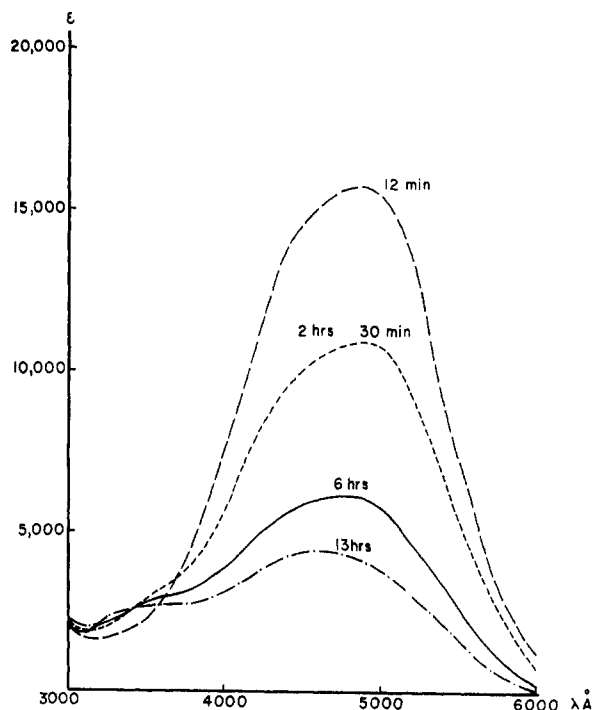

o——o   ℰ max of optical spectrum in presence of PbO₂

□——□   ℰ max of optical spectrum without PbO₂

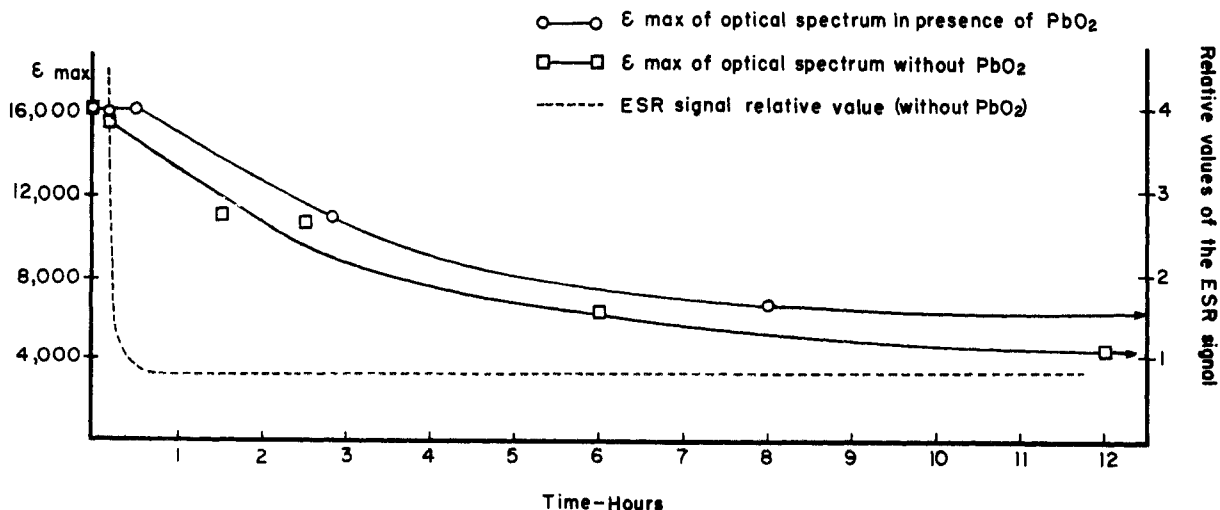-------   ESR signal relative value (without PbO₂)

Fig. 12.—DECAY OF QUINONE AND RADICAL AS A FUNCTION OF TIME ($^1/_{10}$ MOL./L.)
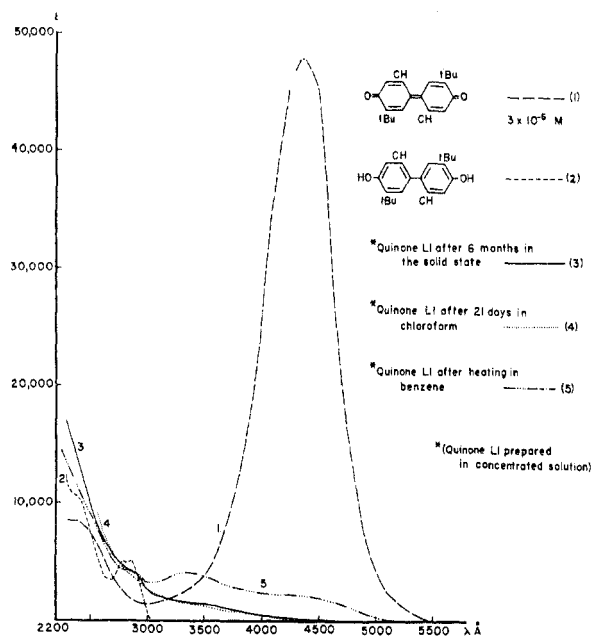
FIG. 13.—SPECTRA IN ETHER. Compounds of transformation of hindered quinone, compared to hindered quinone and hindered biphenol.

as two ortho-methyl groups in diphenoquinone provide sufficient steric hindrance to coplanarity to raise the energy of the quinone to the point where there is an appreciable amount of oxygen diradical in equilibrium with it at room temperature. Presumably if the reactivity of the oxygen diradical could be further reduced by two additional ortho-t-butyl groups it should be possible to obtain the diradical in appreciable amounts. In fact, such a diradical should exceed in stability the phenoxy monoradicals of Muller and Cook.

EXPERIMENTAL

Preparation of 3,5-dichloro-4-iodonitrobenzene.[18] A solution of 50 g. of 2,6-dichloro-4-nitroaniline (Kodak) in 165 cc. concentrated sulfuric acid was cooled to 0°C. To another 165 cc. of concentrated sulfuric acid were slowly added 17.5 g. NaNO₂, care being taken to keep the temperature below 40°, and the resulting solution of nitrosylsulfuric acid was cooled to 0°C. The two solutions were mixed and allowed to stand 0.5 hr. Then, 600 cc. of H₃PO₄ (85%) were added at such a rate as to keep the temperature below 5°C. (1.5 hr.). The yellow solution was allowed to stand 0.5 hr. at 0°, 1 g. of urea was added, and the solution was poured into one liter of ice water containing 42 g. of potassium iodide. The decomposition of the diazo compound produced much foam, and the iodo compound precipitated as a light brown product. After 1 hr. the precipitate was filtered, washed with water, and recrystallized from alcohol. Yield: 63 g. (82%), m.p. 151–153°.

2,2',6,6'-Tetrachloro-4,4'-dinitrodiphenyl. This compound had previously been prepared by Ridge[19] by deamination of 2,6-dichloro-4-nitroaniline, but with poor yields. A different procedure was used: 40 g. of 3,5-dichloro-4-iodonitrobenzene were melted in a large test tube at 240–250°, and 0.5 g. of

bronze copper was added. The reaction caused the mixture to boil and it was sometimes necessary to cool it. The rest of the copper (15 g.) was slowly added over a period of 0.5 hr., the temperature being kept at 250–260°. The mixture was extracted, while still hot, with boiling benzene. The solution was chromatographed on alumina to eliminate the tars. The product obtained was contaminated with a yellow oil and was recrystallized from AcOH, yielding 9.5 g. of yellow crystals (37%), m.p. 181–182°.

2,2',6,6'-Tetrachlorobenzidine. This compound had been previously prepared by benzidine rearrangement[20,21] of 3,3',5,5'-tetrachlorohydrazobenzene with H₂SO₄ in very poor yield. An attempt to prepare this compound by the reduction of the 2,2',6,6'-trichloro-4,4'-dinitrodiphenyl by zinc and acid (AcOH, HCl) in various solvents (AcOH, EtOH) gave a product which was impossible to crystallize. However, catalytic hydrogenation (PtO₂) of this product gave a pure crystalline benzidine in good yield. The hydrogenation was carried out using 390 mg. PtO₂, 600 mg. dry Na₂SO₄, 200 cc. cyclohexane, and 2 g. of the dinitro compound. The theoretical quantity of hydrogen was taken up in 2 hr., giving a light yellow solution. The catalyst was filtered off, washed several times with ether, and then the combined solutions were concentrated; 1.37 g. of tetrachlorobenzidine (light yellow needles) were obtained. Yield: 81%, m.p. *ca.* 207°. After purification, the melting point was raised to 212–213°. The benzidine gave a dihydrochloride and a diacetyl derivative (acetylation with acetic anhydride and pyridine on a steam bath, crystallization from AcOH), m.p. 314°. Titration of the diamine was done by acetylation.[22] Result: 1.98 amino groups.

Anal. Calcd. for C₁₂H₈Cl₄N₂: C, 44.75; H, 2.5; Cl, 44.04; N, 8.69. Found: C, 45.03; H, 2.74; Cl, 42.64; N, 8.97.

Diacetylated derivative. Calcd. for C₁₆H₁₂Cl₄N₂: C, 47.31; H, 2.97; Cl, 34.92; N, 6.89. Found: C, 47.52; H, 2.95; Cl, 34.70; N, 7.03.

2,2',6,6'-Tetrachloro-4,4'-biphenol. The diamine (1 g.) was dissolved in concentrated H₂SO₄ (20 cc.) and cooled to 0°C. NaNO₂ (450 mg.) was slowly dissolved in concentrated H₂SO₄ (20 cc.) at a temperature below 40°C. The two solutions were mixed at 0°C., 35 cc. H₃PO₄ (85%) were added slowly so that the temperature remained below 5°C. After 1 hr., this solution was poured into aqueous H₂SO₄ (110 cc. acid for 140 cc. water), and the acidic solution was boiled 12 min. and then poured onto ice. A precipitate was obtained and the product was extracted from the suspension with ether; the ether solution was then extracted several times with 5N NaOH, and the product was precipitated from the reddish alkaline solution by the addition of dilute HCl. The product obtained was extracted with ether, the resulting ether solution was washed with water, dried, and the ether was removed under vacuum. A yellow oil was obtained which crystallized slowly. The crude product was purified by sublimation (160°/1 mm.). Yield: 760 mg. (76%), m.p. 185–186°, after resublimation, 186°.

Anal. Calcd. for C₁₂H₆Cl₄O₂: C, 44.48, H, 1.86; Cl, 43.77. Found: C, 44.55; H, 2.01; Cl, 43.75. The titration of the tetrachlorophenol by alkali gave 1.98 phenolic hydroxyl groups.

Diacetyl derivative (pyridine, acetic anhydride, purification in acetic acid), m.p. 164–165°.

2,2',3,3',5,5',6,6'-Octachloro-4,4'-biphenol. This compound (XXV) has been described by Smith[11] (XXV) but it is believed to be a mixture of different octachlorobiphenols. Here, a different method of preparation was used. The tetrachlorobiphenol (0.5 g.) was dissolved in CHCl₃ (30 cc.). A rapid current of chlorine was passed through the solution

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(18) H. A. J. Schoutissen, *J. Am. Chem. Soc.*, **55**, 4531 (1933).

(19) D. Ridge, *J. Chem. Soc.*, 734 (1947).

(20) F. L. W. van Roosmalen, *Rec. trav. chim.*, **53**, 375 (1934).

(21) R. B. Carlin and W. D. Forshey, *J. Am. Chem. Soc.*, **72**, 793 (1950).

(22) S. Siggia, *Quantitative Organic Analysis Via Functional Groups*, John Wiley and Sons, Inc., New York, 1949, p. 5.

for 10 min. The excess chlorine and chloroform were removed under vacuum. The crystalline residue was purified by sublimation (200°/1 mm.), to give 660 mg. (95%), m.p. 237–237.5°; pure product, m.p. 238°.

Anal. Calcd. for $C_{12}H_2Cl_8O_2$: C, 31.2; H, 0.43; Cl, 61.4. Found: C, 31.07; H, 0.69; Cl, 61.42.

The diacetyl derivative was prepared with hot acetic anhydride and a drop of H_2SO_4 and recrystallized from acetic acid, m.p. 195°.

Anal. Calcd. for $C_{16}H_6Cl_8O_4$: C, 35.2; H, 1.1; Cl, 51.96. Found: C, 35.36; H, 1.27; Cl, 51.84.

2,2',3,3,3',3',5,5',6,6'-Decachloro-3,3',4,4'-tetrahydro-4,4'-diketodiphenyl.—The tetrachlorobiphenol (250 mg.) was dissolved in acetic acid (25 cc.) and a rapid current of chlorine was passed through the hot solution until it was saturated (0.5 hr.). Then 7 cc. of water were added and a crystalline product precipitated on cooling. The product was washed with water and dried. Yield: 390 mg. (96%), m.p. 190–191°. It was recrystallized from boiling acetic acid-water, m.p. 191.5–192°. It is soluble in AcOH, ether, $CHCl_3$, less soluble in alcohol.

Anal. Calcd. for $C_{12}Cl_{10}O_2$: C, 27.15; H, 0; Cl, 66.81. Found: C, 27.27; H, 0.45; Cl, 66.46.

This product could be obtained also by action of the same reagent (chlorine in AcOH) on the octachlorobiphenol with a yield of 92%.

Reduction of the decachloro compound (XXXIII). (1) By Zn and AcOH: 24 mg. of the compound were dissolved in 1 cc. acetic acid. The solution was decolorized by boiling for 2 min. in the presence of zinc powder. Two cc. of water were added to precipitate the product. Yield: 91%, m.p. 234°. (2) By alcohol: This reaction has been studied by U.V. as a function of time. The decachloro compound (4.8 mg.) was dissolved in 50 cc. of alcohol and the U.V. spectrum was taken from time to time. The reaction was complete after 24 hr. The same behavior toward alcohol has been observed with the hexachlorophenol, but the reaction was much slower (about 280 hr.).

Action of silver on the decachloro compound (XXXIII). The active silver was prepared by reduction of AgCl in alkaline solution of hydroxylamine.[7] The reaction was carried out under nitrogen free from oxygen in anhydrous benzene, which had been dried by distillation from metal cetyl of benzophenone. The nitrogen was purified by passing through Fieser's solution, through an aqueous solution of lead acetate, through concentrated H_2SO_4, and finally through a solution of metal cetyl of benzophenone in ether. The blue color of the ether solution indicated the absence of oxygen and water.

In a two-armed flask was placed a solution of 50 mg. of the decachloro compound in 25 cc. of benzene and 500 mg. of active silver. Nitrogen was bubbled through the suspension for 0.5 hr. Then the flask was cooled at −80°C., the two arms were sealed, and the flask was shaken for 16 hr. at room temperature. No reaction seemed to have occurred. The silver was filtered off, washed with ether, and the solvents were removed to give a yellow crystalline substance. The U.V. spectrum showed that this compound was the unchanged starting material. Heating a mixture of the decachloro compound with active silver under vacuum (200°/1 mm.) resulted only in sublimation of the starting material.

Attempts to prepare the 3,3'-dibromo-2,2',3,3',5,5',6,6'-octachloro-4,4'-diketo-3,3'-4,4'-tetrahydrodiphenyl. (1) The addition of bromine to a boiling methanol solution left the octachlorobiphenol unchanged. (2) The addition of bromine to a cold or boiling acetic acid solution of biphenol gave no reaction. (3) The addition of bromine to an acetic acid solution of biphenol in the presence of a 15% excess of sodium acetate at 10° for 12 hr. gave no crystalline products. (4) Reaction (3) was carried out with twice the quantity of sodium acetate for 8 days. A yellow precipitate, insoluble in alcohol, chloroform, benzene, boiling acetic acid, and water, was slowly formed. This product did not melt at 310° and could not be sublimed. It was probably polymeric.

2,2',6,6'-Tetrachloro-3,3',5,5'-tetrabromo-4,4'-biphenol. Fifty mg. of tetrachlorobiphenol were dissolved in 5 cc. N NaOH. To this solution 100 mg. of bromine in 10 cc. N NaOH were added. The yellow solution was rapidly decolorized. After 0.5 hr. it was neutralized and extracted with ether. After removal of the ether, the residual oil crystallized slowly and was sublimed at 200°/1 mm., m.p. 251–252°. The product was recrystallized from aqueous alcohol (50%), m.p. 257–258° with decomposition.

Anal. Calcd. for $C_{12}H_2Br_4Cl_4O_2$: C, 22.4; H, 0.32; Br, 49.80; Cl, 22.18. Found: C, 22.75; H, 0.49; Br, 48.2; Cl, 21.5.

(Bromine was calculated assuming that the molecule contained four chlorines.)

Attempts to prepare the 3,3',5,5'-tetrabromo-2,2',3,3',6,6'-hexachloro-4,4'-diketo-3,3',4,4'-tetrahydrodiphenyl. (1) Action of an excess of chlorine on the biphenol in an acetic acid solution at room temperature gave the decachloro compound previously described. (2) The technique of Muller,[7] i.e., action of chlorine in a solution of biphenol in MeOH, AcOH at −20°C. yielded 99% of the decachloro compound.

2,2'-Dimethyl-4,4'-dinitrodiphenyl. This compound was prepared according to the procedure of Sherwood and Calvin.[23] The product was recrystallized from ethanol in the presence of charcoal. Yield: 30%, m.p. 170°.

2,2'-Dimethylbenzidine hydrochloride. This product was prepared by two methods: (1) By reduction of 2,2'-dimethyl-4,4'-dinitrodiphenyl. Nine hundred mg. of dinitro compound were dissolved in 25 cc. ethanol. Then HCl and Zn were added to the boiling solution until the reduction was complete (1.5 hr.). The solution was neutralized with Na_2CO_3 and extracted with ether which was evaporated to dryness. The residue from the ether extract was dissolved in dilute HCl and the hydrochloride was precipitated by the addition of concentrated HCl. Yield: 60%. (2) Preparation according to the method of Schultz and Rohde[24] and purification as above. Yield: 80%.

Anal. Calcd. for $C_{14}H_{16}Cl_2N_2$: C, 58.95; H, 6.36; Cl, 24.86; N, 9.82. Found: C, 59.11; H, 6.27; Cl, 24.66; N, 9.75.

2,2'-Dimethyl-4,4'-biphenol. This compound was prepared according to the method of Brockmann and Dolars[25] and recrystallized from benzene. Yield: 90%, m.p. 116°.

2,2'-Dimethyl-5,5'-di-t-butylbiphenol.[15] Two g. of dimethyl-2,2'-biphenol were dissolved in 70 cc. benzene at 60–70°, then 0.1 cc. of concentrated sulfuric acid was added and isobutylene passed through the solution by means of a sintered glass bubbler for 6 hr.

The solution was washed three times with 2N NaOH, dried and concentrated. The resulting crystalline colorless product was contaminated with an oil which was absorbed by pressing the product between filter paper. The white crystals (1.75 g.) obtained were sublimed at 170–200° under 1 mm. Yield: 1.3 g. (41%), m.p. 213–214°.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.9; H, 9.26. Found: C, 81.05, 81.09; H, 9.65, 9.04.

This biphenol is soluble in benzene, ether, and insoluble in 2N NaOH.

Oxidation of biphenols. Solvents used: Benzene, purified as indicated above; ether, anhydrous Merck, dried over sodium, then distilled and kept over sodium; water, distilled; acetic acid, analytical reagent. Nitrogen was free from oxygen (see above).

(1) Oxidation by active lead dioxide in moist ether at 0°.[5] The lead dioxide used here and in the following experiments was prepared according to the technique of Kuhn and Hammer[26] by hydrolysis of lead tetraacetate.

Technique of oxidation and results: 10–15 mg. of phenol were dissolved in 25 cc. of moist ether, cooled at 0°, then

(23) D. W. Sherwood and M. Calvin, *J. Am. Chem. Soc.*, **64**, 1350 (1942).

(24) G. Schultz and G. Rohde, *Chem. Zeit.*, *II*, 1447 (1902).

(25) H. Brockmann and A. Dorlars, *Ber.*, **85**, 1180 (1952).

(26) R. Kuhn and I. Hammer, *Ber.*, **83**, 413 (1950).

shaken at 0° with 1 g. lead dioxide for 5 min. The following results were obtained:

p-Cresol	Weak violet coloration, disappearing in a few minutes
p-Methoxyphenol	Strong blue coloration, disappearing in 20–25 min.
XLII	No coloration, but polymers
XXVI	No coloration
XXXII	No coloration
Pentachlorophenol	No coloration
XLIX	Deep red coloration, stable several hours

(2) *Oxidation by silver oxide*, prepared according to Willstatter[12] in anhydrous ether with dry sodium sulfate.

(3) *Oxidation by lead dioxide*, prepared as above, in anhydrous ether or benzene, in air or under nitrogen.

(4) *Oxidation with potassium ferricyanide in alkaline solution*.[7] The reaction was carried out in a 100 cc. two-necked flask with 100 mg. biphenol in 15 cc. benzene. The flask was cooled to −80° and then a solution of 1 g. potassium ferricyanide in 5 cc. 2N KOH was added under nitrogen. Nitrogen was passed through the flask for 15 min., then the flask was sealed and shaken at room temperature. Results of the reaction were observed by U.V. spectroscopy.

Oxidation of 2,2'-dimethyl-5,5'-di-t-butylbiphenol. In all the experiments a large excess of lead dioxide (5 to 10 times) was used.

Spectral and ESR studies on solutions. (1) $c = 3 \times 10^{-5}$ mol./l.: A solution of biphenol in benzene or ether (Curve 1, Fig. 3 and Curve 1, Fig. 13) was shaken with lead dioxide directly in the quartz cell of the spectrophotometer for 2 to 30 min. Then the cell was centrifuged for a few minutes and the optical spectrum was taken immediately. The reaction was complete after 2 min. The same results were obtained when the experiment was carried out in an atmosphere of nitrogen.

(2) $c = 10^{-3}$ mol./l. (Curve 2, Fig. 3): A special apparatus (Fig. 14a) was designed which made it possible to use the same sample of solution for optical and ESR spectra. The solution was free from lead dioxide and oxygen. The thickness of the borosilicate optical cell was 0.25 mm. After introducing the solution of biphenol into the flask, the apparatus was sealed at *a* under high vacuum and the solution was frozen in liquid nitrogen. Then the apparatus was tilted in such a way as to allow the iron weight, *d*, to break the thin wall, *c*. The liberated lead dioxide was poured onto the frozen solution, the flask was sealed at *b* and the solution was heated up to room temperature. After shaking the solution 2 min., the lead dioxide was centrifuged and by turning the apparatus upside down the solution filled the optical cell, *e*, and the side arm, *f*, making it possible to take the optical spectrum through *e* and the magnetic signal on *f*. Result: $\lambda_{max} = 4450$ Å, $\epsilon_{max} = 39,600$. ESR signal: 1 electron for 1000–2000 molecules. By shaking a longer time (5, 10, 30 min.) a decrease of ϵ_{max} was observed, but there was no appreciable change in the ESR signal, indicating that the reaction was complete in less than 2 min.

(3) $c > 10^{-3}$ mol./l.: Reactions were carried out under vacuum in the apparatus shown in Fig. 14b. After shaking 15 min. (enough time to insure a complete reaction in all cases) the apparatus was centrifuged at 1000 rpm for 1 min. and the red solution decanted into the side arm where the ESR measurement could be taken directly. To take the optical spectrum the apparatus was opened at *a* and an aliquot of the solution was rapidly diluted with the adequate amount of benzene previously placed in the cell of the spectrophotometer (Curves 3, 4, 5, Fig. 3, Fig. 4, Fig. 11, Fig. 12).

(4) Titration of the solution (10^{-2}–10^{-3} mol./l.): The oxidation was carried out by shaking the benzene solution with potassium ferricyanide and 2N sodium hydroxide for 15–30 min. The solution was washed with water and an aliquot was added to sodium iodide in acetic acid, whereupon the color of the solution changed from red to orange. This solution was titrated with 0.10N sodium thiosulfate. Results: 0.24, 0.4, 0.44, 0.42 oxidation equivalents per molecule. The first measurement was made under pure nitrogen. Theory for the quinone LI, 2 equivalents; for the dimer, 1 equivalent; for the trimer, 0.66 equivalents.
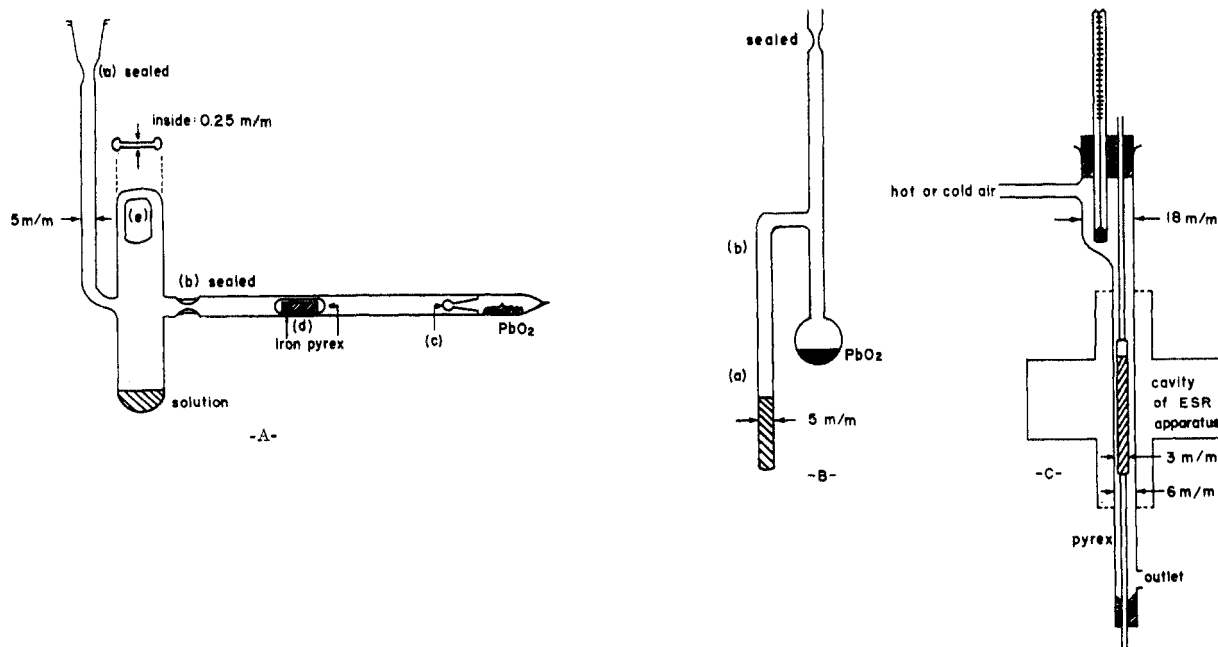

FIG. 14

(A) Apparatus to study ESR signal and optical spectrum of the quinone LI in dilute solution under vacuum. (B) Apparatus to study ESR signal of quinone LI in concentrated solution. (C) Equipment for temperature dependency study of the hindered polymeric quinones

Action of p,p'-biphenol on the hindered diphenoquinone LI (Fig. 6a). The diphenoquinone LI was prepared by shaking a benzene solution of the hindered biphenol ($3 \times 10^{-5} M$) with lead dioxide for 4 min. The orange solution ($\Sigma_{max} = 44,500$) was added to an ether solution of biphenol (3 mol. for 1 mol.). The spectrum of the resulting solution was taken from time to time until the completion of the reaction.

The concentration of quinone LI was calculated from the initial amounts of hindered biphenol. The amount of the diphenoquinone produced was calculated from the Σ of the absorption band.

Action of p,p'-biphenol on the polymeric diphenoquinones. The quinones were prepared by shaking under vacuum for 15 min. a benzene solution of hindered biphenol (0.01M) with lead dioxide (Fig. 6b). An aliquot of the resulting solution was diluted 1000 times and added to the same volume of an ether solution of biphenol (7 mol. per mol. of initial hindered biphenol). The reaction was followed by U.V. spectrum as above. Calculations were made on the same basis.

Action of hindered biphenol XLIX on the hindered quinone LI (Figs. 7 and 8). The quinone LI was prepared in dilute solution as above (Curve 1, Fig. 8). Its decay in benzene (Curve 1, Fig. 7) was followed by the decrease of the ϵ_{max} at 4440 Å (Curve 4, Fig. 8): 20 cc. of a solution of diphenoquinone LI ($c = 3.07 \times 10^{-5}$) was mixed with 10 cc. of a solution of the hindered biphenol (same concentration). By heating the reaction mixture at about 60° for 40 min. there was a 90% decrease in the absorption band, then the solution was shaken for 2 min. with lead dioxide and the spectrum was taken again.

Temperature dependency study (Fig. 10). The reaction was performed in an apparatus similar to *B* (Fig. 14) having a side arm of 3 mm. diameter. The side arm was sealed off and placed in the apparatus, *C*, as is shown in Fig. 14. The apparatus was previously standardized with a thermocouple. The heating system consisted of a hot stream of air at various temperatures. The intensity of the ESR signal and the corresponding temperatures were recorded.

Red glass. (1) Oxidation with lead dioxide: 100 mg. of biphenol were dissolved in 30 cc. of benzene and the mixture was shaken in the presence of 2 g. of lead dioxide for 15 to 30 min. After centrifugation the solvent was removed under vacuum at room temperature (10–20°), giving a red glass which was left 2 hr. under 1 mm. pressure before analysis.

Oxidation under nitrogen: The apparatus was composed of two flasks connected by a piece of sintered glass to filter the lead dioxide (Fig. 15). After the apparatus had been
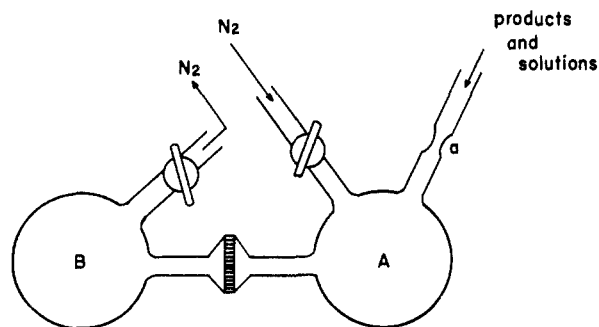

FIG. 15.—APPARATUS TO PREPARE THE HINDERED DIPHENOQUINONE IN THE SOLID STATE BY OXIDATION WITH LEAD DIOXIDE

filled with pure nitrogen and sealed at *a*, the reaction was performed in flask *A*, the solvent was filtered into flask *B* by pressure of the nitrogen; keeping *B* at 10° and freezing *A* at −80°, under vacuum, the benzene was distilled in *A*. A red glass was obtained in *B* and dried under 1 mm. pressure.

(2) Oxidation with potassium ferricyanide: The same solu-

tions of biphenol were used. The oxidant was a solution of 2 g. of potassium ferricyanide in 20 cc. of 2N sodium hydroxide. The two solutions were shaken together for 15 to 30 min. and the layers were separated. The benzene layer was washed with water, dried over sodium sulfate, and evaporated at room temperature under vacuum, giving a red glass.

Oxidation under nitrogen (pure nitrogen was bubbled through all solutions and solvents before using them): The reaction was carried out in a special separatory funnel (Fig. 16) filled with nitrogen and kept at 10°. After shaking
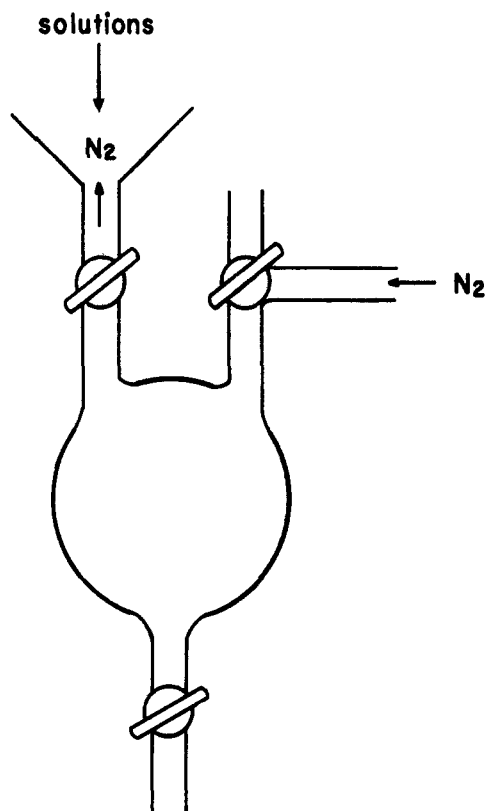

FIG. 16.—APPARATUS TO PREPARE THE HINDERED DIPHENOQUINONE IN THE SOLID STATE BY OXIDATION WITH FERRICYANIDE

in the separatory funnel for 30 min. the layers were separated; the red benzene layer was washed with boiled water, then dried over sodium sulfate in an apparatus (Fig. 15) filled with nitrogen; it was then filtered and evaporated as indicated above, giving the same red glass.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.43; H, 8.69. Found: (A) C, 80.05; H, 8.67. (B) C, 81.67; H, 8.72. (C) C, 80.20; H, 8.93. (D) C, 80.39; H, 8.93.

(A) was prepared by oxidation with lead dioxide in the presence of air and dried at room temperature. (B) was prepared by oxidation with potassium ferricyanide under nitrogen and dried at 35°. (C) was prepared by oxidation with potassium ferricyanide under nitrogen and dried at room temperature. (D) was prepared by oxidation with lead dioxide under nitrogen and dried at room temperature.

3,3'-Dimethyldiphenoquinone. This compound was prepared by boiling a solution of 3,3'-dimethylbiphenol (34 mg.) in 2 cc. of benzene with lead dioxide (700 mg.) for 5 min. The lead dioxide was separated and extracted several times with boiling benzene. The resulting orange solution was concentrated to 5 cc., yielding 15 mg. of quinone (dark red needles); $\lambda_{max} = 4090$ Å; $\epsilon_{max} = 65,000$ (benzene).

Diphenoquinone. This compound was prepared from p,p'-

biphenol using the procedure described above. Dark orange needles resulted; λ_{max} = 3985 Å; ϵ_{max} = 53,200 (benzene).

Steric Considerations in Base Catalyzed Condensation; The Darzens Reaction[1]

HAROLD KWART AND LEWIS G. KIRK

The Darzens condensation of benzaldehyde and choloroacetone has been carried out in good yield. The exclusive glycidic ketone product of this reaction has been shown by a synthetic procedure to have the *trans* arrangement of substituents on the oxide ring. The significance of this observation for the mechanism of the Darzens reaction in particular and aldol condensations in general is discussed. Circumstances are considered under which it is possible to obtain the *cis* isomer.

Ballester[2] has very recently reviewed the evidence that strongly points to a mechanism involving an alpha halogenohydrin anion as intermediate in the Darzens condensation[3] and indicates that the course of oxirane ring formation from this intermediate requires Walden inversion at the halogen bearing carbon atom. Further, the rate determining step in the over-all reaction has been deduced[4] to be the slow formation of this intermediate. The self-condensation[5] and cross-condensation[6] of phenacyl halides have afforded both *cis* and *trans* (substituted) benzalacetophenone oxides depending on the conditions of reaction. The respective structures of these isomers have been assigned on the basis of spectral characteristics and stereospecific chemical reactions.

The mechanism discussed by Ballester[2,7] has not considered the possibility of two diastereomerically related (*cis* and *trans*) intermediate anions; nor has the possibility been suggested that the occurrence of the two isomers in a given Darzens reaction may correspond to the possible formation of two discrete intermediates. In the present investigation we have shown that with simple Darzens reagents the condensation produces only one of the two possible oxiranes. We have determined the configuration of this product and attempted to generalize the significance of its exclusive formation.

RESULTS AND DISCUSSION

The Darzens condensation of benzaldehyde and monochloroacetone, using sodium methoxide in absolute methanol solution as the base, gave only one epoxyketone product. The composition of the product did not vary with the time and temperature of reaction though the yield of undistillable residue was increased beyond a certain optimum adjustment of these variables. The sharp melting, crystalline product was shown to possess the *trans* relationship of the substituents on the oxide ring by synthesis through an established procedure.

Benzalacetone, prepared by cross-aldol of acetone and benzaldehyde, was identified to have the *trans* configuration, (characteristic of the products of base catalyzed condensation reactions),[8] by its facile conversion through sodium hypochlorite oxidation to the known *trans* cinnamic acid. Additional proof of its configuration was afforded by the presence of a strong band in the region 10.2–10.6 microns.[9] Reduction with lithium aluminum hydride

(1) Part of this work is obtained from the Thesis of Lewis G. Kirk, presented in partial fulfillment of the degree of Master of Science at the University of Delaware.

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(8) (a) S. E. Boxer and R. P. Linstead, *J. Chem. Soc.*, 740 (1931). (b) R. P. Linstead, E. G. Noble and E. J. Boorman, *J. Chem. Soc.*, 557 (1933).

(9) This absorption has been ascribed to out-of-plane deformation of the two hydrogens attached to the *trans* double bond, a corresponding mode being absent in the *cis*. See particularly R. S. Rasmussen, R. R. Brattain and P. S. Zucco, *J. Chem. Phys.*, **15**, 135 (1947); N. Sheppard and G. B. B. M. Sutherland, *Proc. Roy. Soc.*, **A196**, 195 (1949). The correlation has previously proven valid for a large variety of substituted olefins and has been accepted