[Contribution from the George Herbert Jones Laboratory of The University of Chicago]

THE MECHANISM OF ACTION OF INHIBITORS IN FREE RADICAL INITIATED POLYMERIZATIONS AT LOW TEMPERATURES[1]

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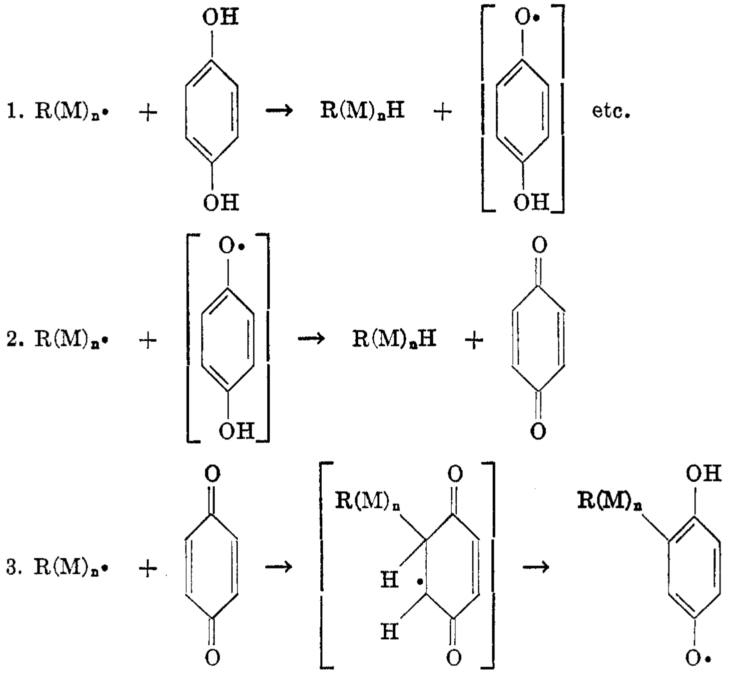
Received August 9, 1954

To obtain useful synthetic polymers in the low temperature emulsion polymerizations of dienes (butadiene, etc.), or the low temperature emulsion copolymerizations of butadiene and styrene, it is necessary to arrest the polymerization at a predetermined state of conversion. The agents commonly used for this purpose are indiscriminately called "inhibitors", "shortstops", "stopping agents", or "terminators". These agents are commonly supposed to destroy the initiating system, or the free radicals generated by the initiating system, or the growing free radicals. The "shortstops" of emulsion polymerizations vary considerably in their effectiveness and in their structure.

Mechanisms have been suggested whereby hydroquinone, catechol (as well as alkyl mono- and di-substituted derivatives of these compounds), chloranil, and polynitro aromatic compounds may act as "shortstops". The effectiveness of the di- and poly-hydroxy aromatic compounds is usually ascribed to their ability to donate a hydrogen atom to a free radical. Schematically, these views are represented as follows:



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[1] The work reported in this paper was done in connection with the Government Research Program in synthetic rubber under contract with the Office of Synthetic Rubber, Federal Facilities Corporation.

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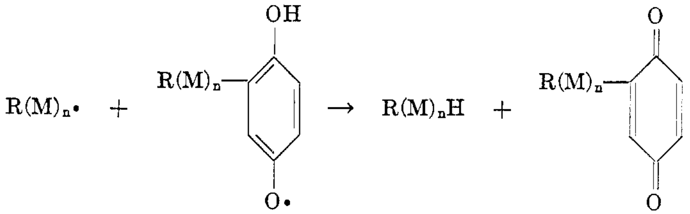

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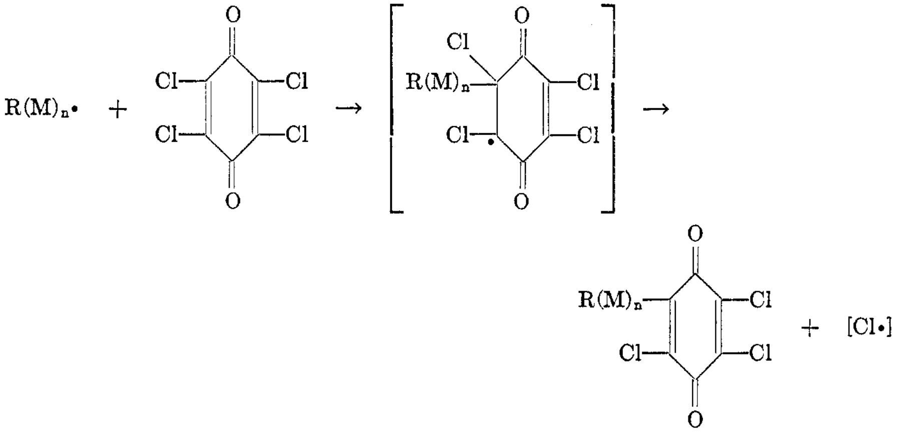
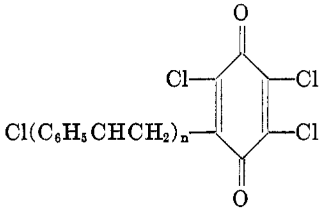


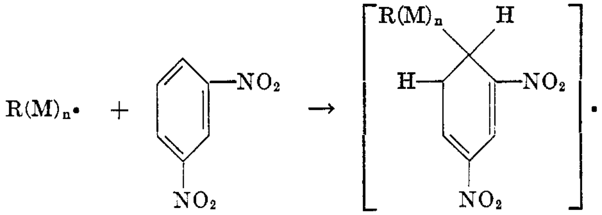
In the case of styrene the product of polymerization is supposed to have the structure given in 6.

6.



1,3-Dinitrobenzene and 2,4-dinitro-1-chlorobenzene presumably function as "shortstops" of polymerization in the manner indicated below.

7.



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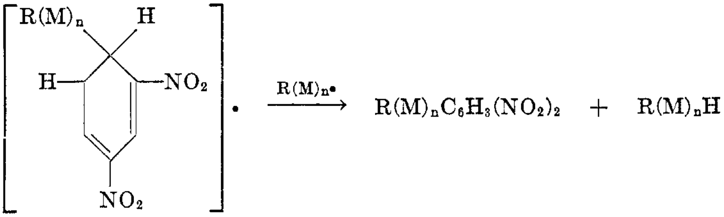


The representations indicated in schemes 1 to 8 are essentially due to Price (1) and his collaborators, and are now widely quoted in the literature (2). Breitenbach and Renner (3) have pointed out that Price's views are inapplicable to the "shortstopping" action of chloranil in the polymerization of styrene. It is also regrettable that many investigators, having adopted Price's formulations, have attempted to extend them without taking cognizance of the fact that the experimental basis for these hypotheses is rather tenuous. Thus, Mark and Tobolsky (2a) state (with regard to the schemes represented in 7 and 8) that "one should observe that the substitution in the benzene ring occurs contrary to the ordinary directing effect of the substituents which are valid in polar and ionic substitution." Such a view presupposes that the structures of the compounds indicated in equation 8 have been unequivocally established. Furthermore, Kolthoff and Bovey (2d) stated that "the radical (indicated in equation 7) is *so much* stabilized by resonance as to be unable to react further with monomer, although it can undergo disproportionation with another radical" (as indicated in equation 8). Essentially similar views have been suggested from time to time by other workers (2c). This conclusion is all the more unfortunate since, without any experimental basis, it suggests that weak dissimilar free radicals tend to disproportionate, rather than to couple.

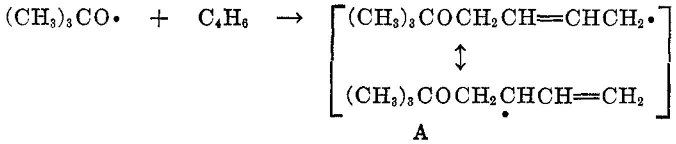
It may be added that to our knowledge, no products similar to those given in equation 8 have ever been isolated from the reaction mixture when *meta*-dinitrobenzene or 2,4-dinitrochlorobenzene are used as "shortstops" in polymerization.

For some years, work has been under way in this laboratory on the mechanism of the "shortstopping" of the low temperature emulsion copolymerization of butadiene and styrene, and on the similar polymerization of butadiene. This work indicates that the schemes suggested by Price (equations 1 to 8) do not adequately represent the mechanism in question. Furthermore, from the work already completed, it is clear that (a) quinone and hydroquinone in the low temperature emulsion polymerization of dienes exert their effect by a common mechanism; (b) chloranil operates by a different mechanism; and (c) dinitrobenzene and 2,4-dinitrochlorobenzene function in still another way. In the present paper, the mechanism of the action of hydroquinone, quinone, methyl hydroquinone, and chloranil will be discussed.[2]

PRESENT WORK

It has been established in this laboratory that *tert*-hydroperoxides (ROOH) react with ferrous salts to give free RO• radicals and that these add to butadiene even at −10° to give products of the following type (4):

9. $(CH_3)_3COOH + Fe^{++} \rightarrow Fe^{++}OH + (CH_3)_3CO\bullet$

10. 

$$(CH_3)_3CO\bullet + C_4H_6 \rightarrow \left[\begin{array}{c}(CH_3)_3COCH_2CH{=}CHCH_2\bullet \\ \updownarrow \\ (CH_3)_3COCH_2\underset{\bullet}{C}HCH{=}CH_2\end{array}\right]$$

A

11. $2\ (CH_3)_3COC_4H_6\bullet \rightarrow$ Mixture of dimers $[(CH_3)_3COC_4H_6C_4H_6OC(CH_3)_3]$

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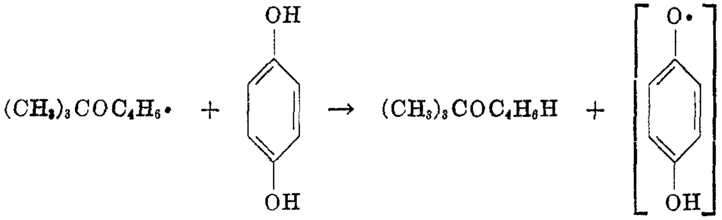
[2] It is obvious that, although particular stress is laid in this paper on the mechanism of

The free radical **A** may be considered as a model of a butadiene polymer free radical $RO(C_4H_6)_n\cdot$ where $n = 1$. The products formed by "shortstopping" this free radical may be taken, therefore, to indicate the mechanism of "shortstopping" free polymer radicals $RO(C_4H_6)_n\cdot$ where n is a large number.

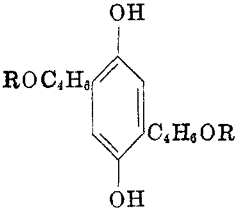
It is most instructive that, if a water solution of a ferrous salt is added to a mixture (maintained at −10°) of water, butadiene, hydroquinone, *tert*-butyl hydroperoxide, and an anti-freeze (methanol or urea), no "dimeric" materials (see equations 9, 10, and 11) are formed. Neither is there any indication of chain-termination of the type proposed by Price. The primary reaction product is

12.

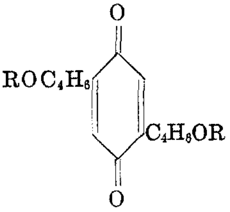


(see equations 1 and 2)

B. However, during the reaction and the isolation, this material is oxidized by the combined action of the air and the iron salts present in solution. The end product, therefore, is 85–95 per cent of **C**.[3] The same compound **C** is isolated



B



C

$R = (CH_3)_3CO\cdot$

when quinone is used as a "shortstop". It should be noted, however, that with both of these reagents the reaction is sluggish and the ferrous ion requirements are rather high [1–10 mole-% on the basis of the $(CH_3)_3COOH$ used]. On the other hand, a very rapid reaction occurs when quinhydrone is used under similar conditions. With this reagent only small amounts of ferrous salts are needed. These results suggest that the effective "shortstop" is neither quinone nor hydroquinone but quinhydrone, and that "shortstopping" is attained by the

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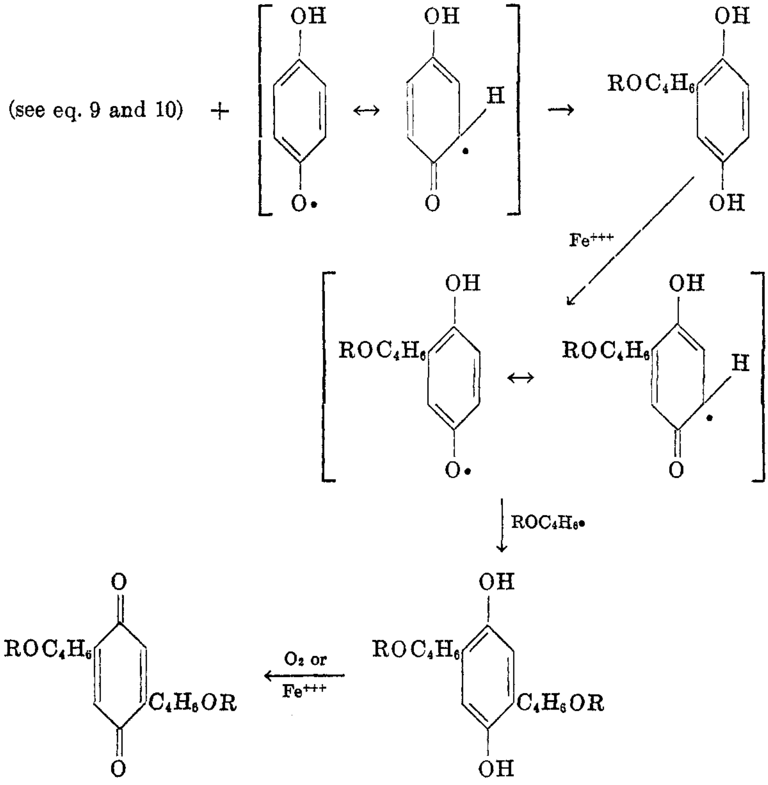
"shortstopping" of low temperature emulsion polymerizations, the views here developed, when properly modified, can be applied to the inhibition of polymerization at higher temperatures and the function of "retarders" of polymerization.

[3] Compound **C** is formed irrespective of considerable variations in the amounts of hydroquinone, quinone, or quinhydrone, or of the *tert*-butyl hydroperoxide used.

"coupling" of the free radical $(ROC_4H_6)\cdot$ with the stable semi-quinone radical. The sequence of reactions may be represented schematically as follows:

13. $ROC_4H_6\cdot$ (see eq. 9 and 10) +



$R = (CH_3)_3C$

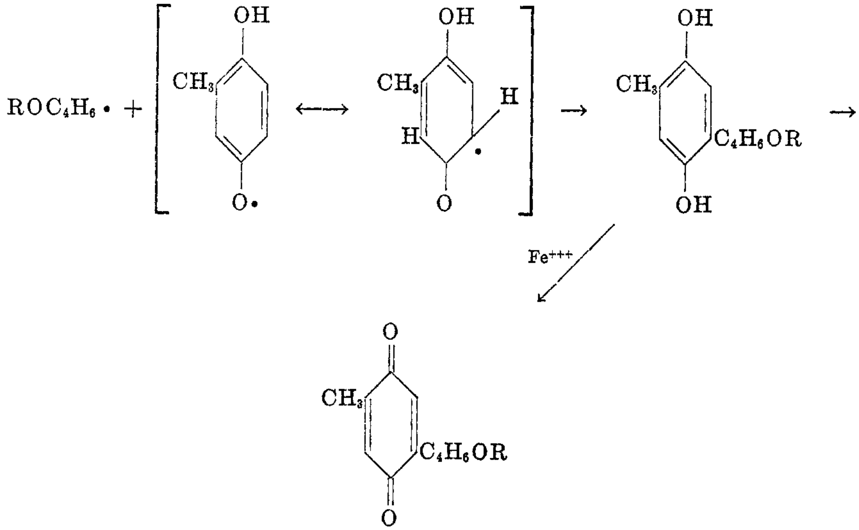
The above experiments suggest that hydroquinone, in order to act as an effective "shortstop", requires the presence of an oxidant, and that quinone requires a reductant. These conditions are usually met when iron salts and a hydroperoxide are used as the initiating system.

As might be expected, even when a large excess of $ROC_4H_6\cdot$ radicals is generated only one $ROC_4H_6\cdot$ radical enters the aromatic ring when toluquinhydrone (an equimolecular mixture of toluquinone and the corresponding hydroquinone) is used as a "shortstop".

From the standpoint here indicated, it would appear that chloranil (tetrachloroquinone) and 2,3,5,6-tetrachlorohydroquinone can not function by the mechanism suggested by Price (eq. 5). Indeed, when a mixture of chloranil and 2,3,5,6-tetrachlorohydroquinone is used, both the termination process and the final product are entirely different from those observed when quinhydrone is used.

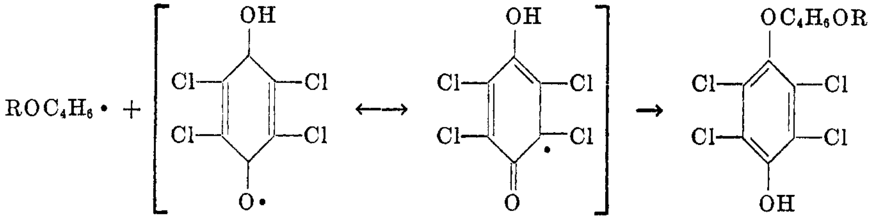
It is noteworthy that the free $RO\cdot$ radicals [$R = (CH_3)_3C—$] generated in solution in the presence of butadiene and a large amount of hydroquinone tend to

14.



D

15.



E

$R=(CH_3)_3C-$

add to butadiene rather than to remove a hydrogen atom from the hydroquinone molecule. In other words, hydroquinone does not destroy the initiating system directly; instead it removes the growing free radicals $RO(M)_n\cdot$, formed from the initiating free radicals $RO\cdot$ and the molecules undergoing polymerization (see equation 10). As a matter of fact, the preponderance of evidence accumulated in this laboratory (some of it still unpublished) indicates that at low temperatures "coupling" of like and unlike weak free radicals[4] is the most important way of terminating polymerization.[5]

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[4] Attention has been called in previous papers [see for instance, Kharasch, Schwartz, and Nudenberg, *J. Org. Chem.*, **18**, 337 (1953)] to the important structural features governing "dimerization" or "coupling" of free radicals. Although [because of multiplicity of factors (steric, polar, etc.)] broad generalizations in organic chemistry are rarely possible, it nevertheless appears that "coupling" in solution is strictly a property of radicals of low reactivity, and that the "dimerization" or "coupling" of resonance-stabilized radicals is directly related to their low reactivity.

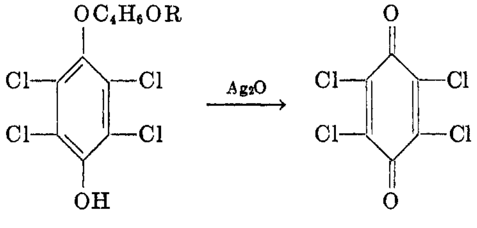
[5] Compare, however, Schmidlin, Wohl, and Thommen, *Ber.*, **43**, 1298 (1910); Ziegler and Orth, *Ber.*, **65**, 628 (1932); Bickel and Waters, *J. Chem. Soc.*, 1764 (1950).

PROOF OF STRUCTURE

The "coupling" of the free radical **A** (produced by the addition of the free *tert*-butoxy radical to butadiene) with the free semi-quinone radical (see equation 13) might give rise to three isomeric compounds of formula **B** or **C** (not counting the *cis* and *trans* isomers of these substances). The complete isolation of the individual compounds was not attempted, since only the skeletal structure of **B** (or **C**) has any bearing on the investigation in question. The skeletal structure of **B** (or **C**) may be readily deduced from the following findings:

1. The molecular weight of **C**.
2. Analysis of **C** for carbon and hydrogen.
3. The fact that in the presence of platinum oxide, one mole of **C** (dissolved in alcohol) absorbs three moles of hydrogen.
4. When **C** is shaken with sodium hydrosulfite, and one mole of the resulting compound (presumably **B**) is hydrogenated in alcohol, only two moles of hydrogen are taken up.
5. Analyses for carbon and hydrogen of compound **B**.
6. Oxidation of **B** by silver oxide to **C**.
7. The presence of the *tert*-butoxy groups in **B** (demonstrated by isolation of *tert*-butyl alcohol, when compound **B**, dissolved in acetic acid, is heated in the presence of a small amount of perchloric acid).
8. Methylation of compound **B** to a dimethoxy derivative.
9. Oxidation of the dimethoxy derivative of **B** with potassium permanganate to the known 1,4-dimethoxyterephthalic acid.

The structure of adduct **E** is surmized on the basis of the following findings: (a) The analyses of **E** for carbon, hydrogen and chlorine; (b) the formation of a mono phenylurethan derivative of **E**, and analyses (C, H, Cl) of this derivative; (c) the formation of chloranil by oxidation with silver oxide.



E

At this point it should be mentioned that when *meta*-dinitrobenzene is used instead of hydroquinone, quinhydrone, or quinone (in the reactions previously cited), no products (equations 7 and 8), similar to the one postulated by Price and others (2) to account for the effectiveness of this reagent, are formed. This fact suggests that *meta*-dinitrobenzene functions quite differently from the agents previously discussed. The mechanism whereby dinitro aromatic compounds may function as "shortstops" in low temperature polymerizations will be treated in a subsequent paper.

EXPERIMENTAL

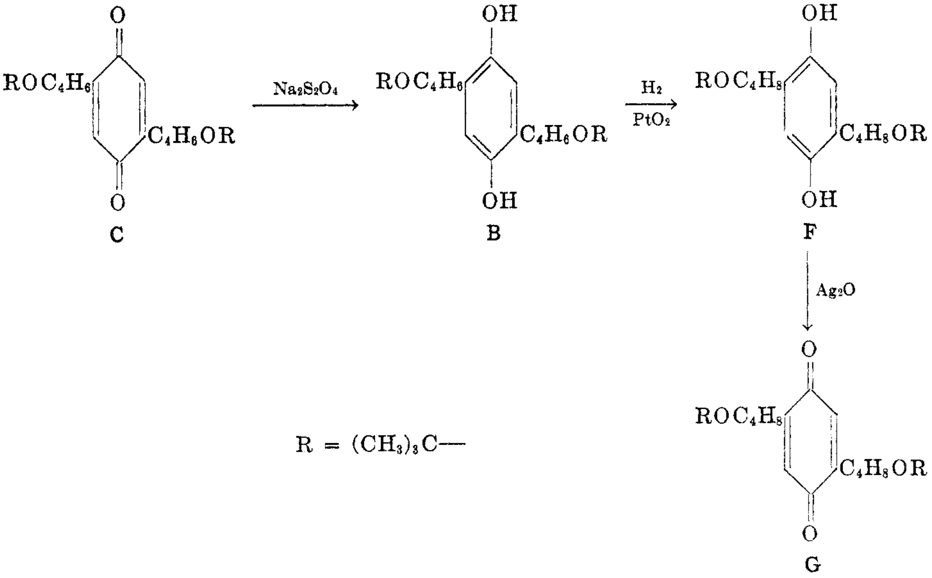
1. *The reaction of hydroquinone with tert-butyl hydroperoxide in the presence of butadiene and iron salts.* To an aqueous solution of urea (100 g. in 150 ml. of water), contained in a three-necked flask and externally cooled to −10°, butadiene (100 ml.), hydroquinone (0.09 mole; 9.9 g.), and *tert*-butyl hydroperoxide (0.18 mole; 16.2 g.) were added. A Dry Ice condenser was used to prevent the loss of butadiene. The air in the apparatus was displaced by nitrogen gas. The whole then was agitated and ferrous ammonium sulfate hexahydrate (0.18 mole; 70.5 g.), dissolved in 250 ml. of water, was added during a two-hour period.

At the end of that time, the cooling bath and the Dry Ice condenser were removed, and the butadiene allowed to escape. The mixture then was extracted with low-boiling ligroin (4 × 1000 ml.), and the extracts were combined. The ligroin extract was washed with saturated salt solution, dried over sodium sulfate, and the ligroin removed by distillation. Residue I, a light-brown oil, weighed 29.7 g.

The aqueous phase, remaining after the ligroin extraction, was extracted with several portions of ether, the extracts were combined, washed with saturated salt solution, dried over sodium sulfate, and, finally, the ether was removed by distillation. Residue II, a dark oil, weighed 5.7 g. (see section 3, below).

The molecular weight of a sample of residue I was 372. The calculated molecular weight for compound C, $C_{22}H_{32}O_4$, is 360. A portion of residue I was dissolved in ethanol and hydrogenated in the presence of PtO_2. The hydrogen equivalent was 124, as compared with the calculated value of 120 for compound C.

A portion of residue I was dissolved in ether and shaken with a water solution of sodium hydrosulfite, the layers were separated, and the ether solution was washed with water. The ether solution then was dried over sodium sulfate and the ether removed.



Anal. Calc'd for compound B, $C_{22}H_{34}O_4$: C, 72.08; H, 10.45.
Found: C, 71.09; H, 10.0.

The residue (corresponding to B) absorbed about two moles of hydrogen gas (Calc'd hydrogen equiv. for B, 180; found, 170) to give F. This hydrogenated material (F), when dissolved in a mixture of ligroin and ethanol (5%), deposited some crystals (about 6% by weight of the starting material) upon cooling. These (F-1) were collected on a filter and when recrystallized melted at 188.5–189.5°. The filtrate (F-2) was reserved for further work.

Anal. Calc'd for compound **F**, $C_{22}H_{38}O_4$: C, 72.08; H, 10.45.
Found: C, 71.83; H, 10.50.

The solid (**F**-1) was dissolved in benzene and oxidized according to Willstatter and Pfannenstiel, *Ber.*, **37**, 4744 (1904). The solid material was collected on a filter, the filtrate shaken with Norit, and the solid collected on a filter. The solvent of the filtrate then was removed at reduced pressure. A yellow crystalline solid, the quinone (**G**), thus was obtained which melted at 48–52°.

Anal. Calc'd for compound **G**, $C_{22}H_{36}O_4$: C, 72.48; H, 9.95.
Found: C, 72.30; H, 9.93.

The solvent of the filtrate (**F**-2) was removed at reduced pressure and the resulting oil was dissolved in benzene. Silver oxide and anhydrous sodium sulfate were added and the whole shaken for two hours. The solid was collected on a filter and the filtrate was shaken with Norit. The filtrate (upon removing the Norit) was evaporated at reduced pressure. A yellow oil was thus obtained (**G**-2).

Anal. Calc'd for compound **G**, $C_{22}H_{36}O_4$: C, 72.48; H, 9.95.
Found: C, 72.08; H, 9.17.

Since it was suspected that this oil contained traces of quinone, the material was treated with steam (15 minutes), and the remaining oil was worked up for analysis in the usual way.

Anal. Calc'd for compound **G**, $C_{22}H_{36}O_4$: C, 72.48; H, 9.95.
Found: C, 72.34; H, 9.51.

Thus, both the solid (**G**-1) and the oil (**G**-2) have the same empirical formula $C_{22}H_{36}O_4$ (**F**-1 and **F**-2 before Ag_2O oxidation likewise must have composition $C_{22}H_{38}O_4$).

The presence of *tert*-butoxy groups in **B** was demonstrated by heating some of the material with 10% hydrochloric acid. The whole was neutralized with $NaHCO_3$. Upon distillation the *tert*-butyl alcohol-water azeotrope was obtained. The presence of *tert*-butyl alcohol was demonstrated by the preparation of a conventional derivative [(4) pg. 1559].

To demonstrate unsaturation in the ROC_4H_6 fragments of compound **B**, some of it was refluxed for one hour with an excess of acetic anhydride to convert to the diacetate. The excess of acetic anhydride and the acetic acid, formed in the reaction, were removed at reduced pressure. The presumed diacetate of **B** was dissolved in ethyl acetate, cooled to −60° and ozonized. About two mole-equivalents of ozone were taken up per mole of the diacetate of **B** (see later for the ozonolysis of the dimethyl ether of **B** and determination of position of alkyl groups in the hydroquinone ring).

No significant change in the product or yield was noted when the molar ratio of hydroquinone to *tert*-butyl hydroperoxide was one to two and two to one. At all times butadiene was used in large excess. When 10 mole-% of ferrous ammonium sulfate was used, results were similar; the products were somewhat easier to work up.

2. *Reaction of quinone with tert-butyl hydroperoxide in the presence of butadiene and ferrous salts.* To an aqueous solution of urea (75 g. in 150 ml. of water), contained in a three-necked flask and externally cooled to −10°, butadiene (1.9 moles), *tert*-butyl hydroperoxide (0.2 mole; 18 g.), and quinone (0.083 mole; 9 g.) were added. A Dry Ice condenser was used to prevent the loss of butadiene. The air in the apparatus was displaced by nitrogen gas. The whole was agitated and ferrous ammonium sulfate hexahydrate (0.2 mole; 78.5 g.), dissolved in 250 ml. of water, added over a three-hour period.

At the end of that time, the cooling bath and the Dry Ice condenser were removed, and the butadiene was allowed to excape. The mixture then was repeatedly extracted with low-boiling ligroin (4 × 1000 ml.), and the extracts were combined. The whole then was shaken with a saturated solution of sodium chloride in water, the organic layer was separated, dried over sodium sulfate, and the ligroin was removed by distillation. Residue I (12 g.) was a light brown oil.

The aqueous phase, remaining after the ligroin extraction, was extracted with several portions of ether, and the extracts were combined, washed with a saturated solution of sodium chloride in water, and the layers were separated. The ether layer was dried with sodium sulfate, and the ether was removed from the filtrate by distillation. Residue II

(15.5 g.) was a light-colored oil. The yield of material (*i.e.* I and II combined) on the basis of the quinone used was 91%.

A small portion of residue I was dissolved in ethanol and treated with hydrogen in the presence of PtO_2. The hydrogen equivalent of this material was 114.5 as compared with a calculated value for $C_{22}H_{32}O_4$ (compound **C**) of 120.

Similarly, residue II had a hydrogenation equivalent of 114, when subjected to the conditions outlined above.

A quantity of residue I was hydrogenated as described above, the PtO_2 was collected on a filter, and the alcohol from the filtrate was removed at reduced pressure. The residue (presumably compound F) was dissolved in a small amount of low-boiling ligroin containing 5% of ethanol. A white crystalline solid (6% by weight of starting material) separated upon cooling of the solution. The crystals were collected on a filter, and crystallized from a mixture of ethanol and ligroin. The material melted at 186–187.5°.

Anal. Calc'd for compound F, $C_{22}H_{38}O_4$: C, 72.08; H, 10.45.
Found: C, 71.73; H, 10.51.

The filtrate, obtained after the removal of the material melting at 186–187.5°, was warmed to 40° and the solvent was removed at reduced pressure. A light-colored oil remained.

Anal. Calc'd for compound F, $C_{22}H_{38}O_4$: C, 72.08; H, 10.45.
Found: C, 72.10; H, 10.45.

Residue II was hydrogenated and worked up in the manner described for residue I. Here, too, a solid was obtained which melted at 187–188°.

Anal. Calc'd for compound F, $C_{22}H_{38}O_4$: C, 72.08; H, 10.45.
Found: C, 72.15; H, 10.54.

The filtrate, upon evaporation at reduced pressure at 40°, gave an oil.

Anal. Calc'd for compound F, $C_{22}H_{38}O_4$: C, 72.08; H, 10.45.
Found: C, 71.91; H, 10.32.

There was no depression in melting point, when the compound melting at 186–187.5° (obtained from residue I) was added to the compound melting at 187–188° (obtained from residue II). Neither of these compounds depressed the melting point of the compound melting at 188–189°, obtained in the experiments with hydroquinone.

A quantity (0.24 g.) of the material melting at 187–188° (compound F) was dissolved in 35 ml. of benzene and shaken with silver oxide. The solid material was collected on a filter, and the solvent of the filtrate was removed at reduced pressure. A solid material was thus obtained which melted at 37–45° (compound G). For analysis of this material see section 1.

Similarly, a quantity of the residue II was oxidized with silver oxide. The oil which resulted was subjected to steam-distillation to remove traces of quinone. The non-distillable yellow oil was extracted with ligroin, the solvent removed and the material dried at reduced pressure.

Anal. Calc'd for compound **C**, $C_{22}H_{32}O_4$: C, 72.48; H, 9.95.
Found: C, 73.07; H, 9.90.

3. *The reaction of quinhydrone with tert-butyl hydroperoxide in the presence of butadiene and ferrous salts.* Insofar as we could determine, the products formed by the action of quinhydrone, *tert*-butyl hydroperoxide, butadiene, and iron salts, namely compound **C** (mixed with some of B), in every respect (mol. wt., hydrogenation equivalent, analyses) are similar to those formed when either hydroquinone or quinone are used. The reaction mixture has been usually worked up in a manner similar that described in Section 1 or 2. The object of the ligroin and ether extractions of the mixture was necessitated since compound **C** but not B is ligroin-soluble. Compound B is, however, ether-soluble. However, as the solution is worked up compound B is oxidized and converted to **C**. At first, we were not aware that these extracts corresponded to the quinone and hydroquinone of a compound of the same skeletal structure and, hence, they were worked up separately.

The yield of **C** and B was about 90% when slightly more than two mole-equivalents of the hydroperoxide was used to one mole equivalent of quinhydrone.

*Preparation of dimethoxy ether of compound **B**.* To an aqueous solution of urea (75 g. in

150 ml. of water), contained in a three-necked flask and externally cooled to −10°, butadiene (1.9 m.), *tert*-butyl hydroperoxide (0.4 m.; 36 g.), and quinhydrone (0.17 m.; 18 g.) were added. A Dry Ice condenser was used to prevent the loss of butadiene. The air in the apparatus was displaced by nitrogen gas. The whole then was agitated and ferrous ammonium sulfate hexahydrate (0.05 m.; 19.6 g.), dissolved in 250 ml. of water, was added over a three hour period.

The reaction mixture was worked up as previously described. From the ligroin extract (mostly compound **C**), upon evaporation of the solvent a light brown oil was obtained which weighed 49 g. (residue I). The ether extract (mostly compound **B**), upon evaporation, gave an additional quantity (6.2 g.) of a brown oil (residue II).

The residue I was dissolved in ether and shaken with a water solution saturated with sodium hydrosulfite. The ether layer was separated, and from the ether filtrate, after evaporation of the ether and treatment with petroleum ether and small amounts of ethanol, a colorless solid separated (1.4 g.), which was collected on a filter. The material melted at 186–187° and it was obviously compound **B**.

The oil which had been separated from the crystals was methylated in the usual manner—with dimethyl sulfate. The resulting mixture was extracted with ether, washed three to four times with sodium hydroxide (10%), then with water, dried over sodium sulfate, and the solvent was removed.

A portion (4.2 g.) of the dimethyl derivative of compound **B** was oxidized by heating with dilute potassium permanganate in the presence of alkali. The precipitated MnO_2 was collected on a filter, and to the filtrate sodium hydrosulfite was added to decompose the unused $KMnO_4$. The solution was then made acid to Congo Red indicator, and the organic material was extracted with ether in a continuous extractor. The ether solution, upon drying with sodium sulfate and evaporation of the filtrate, gave a solid (0.64 g.) which melted at 236–239°. A single crystallization from water raised the melting point to 260–260.5°.

In another oxidation of 5 g. of dimethyl derivative of B, a solid (0.8 g.) was obtained which melted at 263–264°. These acids did not depress the melting point of an authentic sample (m.p. 265–266°) of 1,4-dimethoxyterephthalic acid.

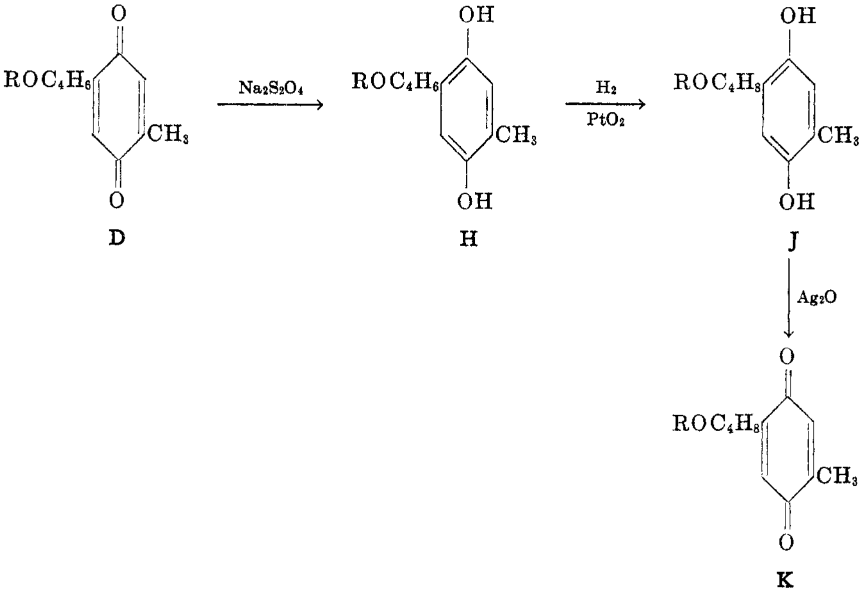
To ascertain the approximate yield one might expect in permanganate oxidations of the type here discussed, the oxidation of 2,5-diallyl-1,4-dimethoxybenzene was studied. About 130 mg. of 1,4-dimethoxyterephthalic acid was obtained from one gram of the starting material.

*Ozonolysis of the 1,4-dimethyl ether of compound **B**.* The 1,4-dimethyl ether of compound **B**, prepared by methylation of **B** with dimethyl sulfate, was ozonized in ethyl acetate. About two mole-equivalents of ozone were taken up. No solid crystalline products were isolated by working up, in the usual way, the reaction product. The presence of formaldehyde as one of the ozonolysis products was demonstrated by the preparation of its methone derivative, which melted at 190° and which did not depress the melting point of a known sample of this compound.

4. *Reaction of toluquinhydrone with tert-butyl hydroperoxide in the presence of butadiene and ferrous salts.* The reaction was carried out in the manner described in Sections 1, 2, and 3. From 9.2 g. (0.07 m.) of toluquinhydrone, 14.4 g. (0.16 m.) of *tert*-butyl hydroperoxide, and 29 g. (0.07 m.) of ferrous ammonium sulfate hexahydrate, we obtained 17 g. of ligroin-soluble material (compound **D**) and about 0.4 g. of ether-soluble compound (presumably mostly **H**). The hydrogenation equivalent of the ligroin-soluble material (compound **D**) was 124.5. This value compares well with the calculated value (124) for conversion of **D** to **J**.

The hydrogenated material (**J**) was oxidized with Ag_2O in the usual way to give **K**. The product was distilled in a molecular still, and the oils, which came over at bath-temperatures, 22–45° (Fraction I) and 45–47° (Fraction II), were collected. The total weight of these oils on the basis of the starting material was 83%.

Anal. Calc'd for Fraction II of compound **K**, $C_{15}H_{22}O_3$: C, 71.96; H, 8.85; Mol. wt., 250.
Found: C, 71.93; H, 9.09; Mol. wt., 247.



The molecular weight of Fraction I was 233, as compared with the calculated value for K of 250.

5. *Reaction of tetrachloroquinhydrone with tert-butyl hydroperoxide in the presence of butadiene and ferrous salts.* The reagents here used were: tetrachloroquinhydrone, 10 g., 0.0406 mole, m.p. 274–277° (from 5 g. of chloranil and 5 g. of tetrachlorohydroquinone); *tert*-butyl hydroperoxide, 0.0812 mole (59% titre); butadiene, 100 g., 1.9 moles; urea, 75 g. in 150 ml. of distilled water; and ferrous ammonium sulfate, 0.024 mole (60 mole-%) in 60 ml. of aqueous solution. The reaction temperature was −10°. The reaction was carried out as in previous cases, except that ferrous solution was added over a period of 4–6 hours. Excess butadiene was allowed to evaporate and the remaining aqueous suspension was extracted with ligroin. The ligroin extract, p-1, was washed and dried in the usual fashion. The aqueous layer, which still contained water-insoluble suspended material, was extracted with ether. The ether extract, e-1, was washed and dried as usual. The aqueous layer was then acidified with hydrochloric acid to solubilize the iron salts; the yellow solid, w-1 (3.6 g.), which remained suspended in the water, was separated by filtration. The remaining aqueous layer was not further investigated.

The yellow solid, w-1, melted at 290° and, when mixed with authentic chloranil, melted at 290°. w-1 was thus chloranil. Additional small amounts of chloranil were obtained from the ligroin and ether extracts (see below). The total amount of chloranil recovered (4.2 g.) corresponds closely to 40% of the tetrachloroquinhydrone used as the starting product. This high recovery of starting product may be due to the low solubility of the reagent in the reaction medium.

The ligroin extract, p-1, was worked up as follows: The more volatile constituents (ligroin, etc.) were removed at water aspirator pressure. To assure complete removal of volatile material from the residual brown oil, rp-1, it was subjected to reduced pressure (0.01 mm.) at room temperature until its weight was constant (7.0 g.). The oil, rp-1, deposited a small amount of ligroin-insoluble yellow crystals which were separated from the oil by addition of ligroin and filtration. The crystals, 0.09 g., appeared to be crude chloranil. The ligroin was removed from the filtrate by evacuation with an oil pump and slight warming (0.03 mm. and 45°). The residual oil, rp-1a, weighed 5.82 g. The molecular weight (cryoscopic in benzene) of the oil, rp-1a, was 389 which is in fair agreement for the molecular weight calculated for the compound **E**, $C_{14}H_{16}Cl_4O_3$, Mol. wt., 374. The oil, rp-1a, upon standing overnight, deposited white crystals, rp-s (1.03 g.), which were separated from oil by addition of ligroin and filtration. The crystals, rp-s, after washing with cold ligroin, melted at 93–96°. After crystallization from ligroin containing about 5% benzene, the product melted at 96–96.5°, and further recrystallizations did not raise the melting point.

Anal. Calc'd for compound **E**, $C_{14}H_{16}Cl_4O_3$: C, 44.94; H, 4.31; Cl, 37.96.
Found: C, 45.37; H, 4.48; Cl, 37.96.

rp-s (m.p. 96–97°) (0.23 g.), dissolved in diethyl ether (20 ml.), was treated with silver oxide and sodium sulfate in the usual fashion. rp-s was thus oxidized to chloranil (0.18 g.). The melting point of the chloranil thus obtained (279–282°) was not depressed by admixture with an authentic sample of chloranil. Furthermore, this material was reduced to tetrachlorohydroquinone (m.p. 238–240°) which did not depress the melting point of a known sample of tetrachlorohydroquinone. No attempt was made to isolate the other fragment of the silver oxide oxidation. In order to show the presence of a hydroxyl group in rp-s (m.p. 96–97°), 0.17 g. was converted to a phenylurethan by treatment in 30 ml. of ligroin with 0.25 g. of phenyl isocyanate in the presence of a trace of pyridine. The product, obtained by extraction with hot ligroin (100°), melted at 131–132°. On recrystallization from ligroin, the melting point was unchanged.

Anal. Calc'd for $C_{21}H_{21}Cl_4NO_4$: N, 2.8. Found: N, 3.1.

Hydrogenation of rp-s (m.p. 96–97°). rp-s (0.1958 g.) in ethanol was quantitatively hydrogenated in the presence of platinum oxide. The hydrogenation equivalent thus obtained was 192. Calculated for the conversion

$$C_{14}H_{16}Cl_4O_3 \xrightarrow{2H_2} C_6H_2Cl_4O_2 + C_8H_{18}O$$

the hydrogenation equivalent is 187. From the hydrogenation reaction mixture there was obtained tetrachlorhydroquinone, m.p. 238–240° (0.16 g.), which gave no depression in melting point when melted with an authentic specimen.

The oil (3.6 g.), which remained after filtration of crystals rp-s (m.p. 96–97°), dissolved in ethanol was hydrogenated in the presence of platinum oxide. The hydrogenation equivalent indicated the oil had approximately the same composition as the solid, namely $C_{14}H_{16}Cl_4O_3$. From the hydrogenation reaction mixture there was obtained, after removal of catalyst and distillation of ethanol, tetrachlorohydroquinone, 2.4 g., which did not depress the melting point of an authentic sample of tetrachlorohydroquinone. It was, therefore, surmized that the oil was a mixture of the 1,4- and 1,2-butadiene adducts to the tetrachloroquinhydrone. The ethanol distillate from the hydrogenation was poured into five times its volume of water and then extracted with low-boiling ligroin. After removal of the petroleum ether by distillation, there remained a small residue (*ca.* 0.6 g.) which boiled from 88–110°, n_D^{20} 1.4134. This fraction gave a positive test for the presence of the *tert*-butyl group (Denigé test) and was assumed to be the ether $C_4H_9OC(CH_3)_3$.

From the ether extract, e-1, after removal of the ether at water pump pressure, there was obtained a residue of yellow crystals, 2.0 g. From these crude crystals was obtained, by crystallization from ether-ligroin, chloranil, 0.5 g. The filtrate from the chloranil, after removal of the ether-ligroin, left a semi-solid residue (1.5 g.). This was not investigated further.

Because of the low water solubility of tetrachloroquinhydrone, the yield of reaction product is quite small. It appears that better yields could be obtained by use of methanol (instead of urea) as an anti-freeze.

SUMMARY

1. It has been demonstrated that a mixture of hydroquinone (quinone, or quinhydrone), *tert*-butyl hydroperoxide, and butadiene react (at low temperature −10°) in the presence of ferrous salts to give in high yields compound **B**, which under reaction conditions is further oxidized to **C**.

2. It has been shown that a mixture of toluquinhydrone, *tert*-butyl hydroperoxide, and butadiene react (at low temperature) in the presence of ferrous salts to give compound **D**.

3. It has been shown that a mixture of tetrachloroquinhydrone, *tert*-butyl hydroperoxide, and butadiene react with ferrous salts to give compound **E**.

4. A mechanism to account for the results cited in 1, 2, and 3 is suggested.

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