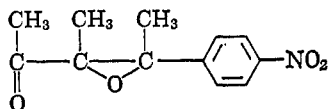


The benzene-hexane filtrate, from which 41% of *cis* isomer (IXb) had been removed, was evaporated. The residue (9 g) consisted of IXa + IXb in about 60:40 proportion, with some *p*-nitroacetophenone as impurity.

Pyrolysis of the Trimethyl Biacetyl-*p*-nitrophenylphosphite Adduct (IXb), *cis*-CH₃CO/C₆H₄NO₂-*p*.—The phospholane IXb (2.0 g) was kept for 16 hr at 120°, under N₂. The resulting brown mixture was dissolved in CCl₄. The H¹ nmr spectrum of this solution showed the three signals of some unreacted adduct IXb at τ 8.37, 8.50, and 8.30. The signals of a small amount of the *trans* isomer (IXa) were present at τ 7.60, 9.12, and 8.53. There were considerable amounts of *p*-nitroacetophenone recognized by the acetyl signal at τ 7.33. The corresponding dissociation product, the biacetyltrimethylphosphite 1:1 adduct (I), was recognized by its singlet at τ 8.20 (CH₃C=O) and by its doublet at 6.50 (CH₃O), $J_{\text{HP}} = 13.0$ cps. There were relatively large amounts of trimethylphosphate (doublet at τ 6.26, $J_{\text{HP}} = 11.0$ cps). A set of signals at τ 7.82, 8.10, and 7.78 could be due to an epoxide.



Reaction of the 1:1 Adduct (I) with α,α,α -Trifluoroacetophenone. Preparation of 2,2,2-Trimethoxy-4 α -acetyl-4 β -methyl-5 α -trifluoromethyl-5 β -phenyl-1,3,2-dioxapholane (Xa) and of the Diastereomer, 5 β -Trifluoromethyl-5 α -phenyl-1,3,2-dioxaphospholane (Xb).—A mixture of 1:1 adduct I (21.0 g, 100 mmoles) and α,α,α -trifluoroacetophenone (17.4 g, 100 mmoles) was kept for 20 hr at 95°. The course of the reaction was followed by H¹ nmr spectroscopy. The mixture was distilled through a 3-in. Vigreux column: (1) forerun, bp 35 to 116° (0.1 mm), 2.5 g; (2) main portion of the two diastereomers Xa + Xb, bp 116–118° (0.15 mm, bath at 165°), n_D^{25} 1.4664, yield 25 g, 85%. A second distillation of Xa + Xb at 0.1 mm (bath at 150–155°) afforded little separation of stereoisomers; the mixture had bp 110–112° (0.1 mm), n_D^{25} 1.4673.

Anal. Calcd for C₁₅H₂₀F₃O₅P: C, 46.9; H, 5.2; F, 14.8; P, 8.1. Found: C, 47.9; H, 5.4; F, 15.2; P, 8.5.

The H¹ nmr spectrum (in CCl₄) gave the signals listed in Table II; integration showed a proportion of 82:18 for the *trans*:*cis*-CH₃CO/C₆H₅ isomers. The P³¹ nmr signals (in CH₂Cl₂) are listed in Table II. The infrared spectrum (in CCl₄) had a C=O band at 5.84 and the strong, split band at 9.22 and 9.40 μ due to the POCH₃ group. A strong characteristic double band was present at 8.40 and 8.60 μ .

Acid-Catalyzed Decomposition of Peroxydienones Derived from Hindered Phenols¹

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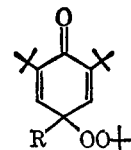
Received March 28, 1966

Decompositions of 4-*t*-butylperoxy-4-methyl-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one (1a) and 4-*t*-butylperoxy-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (1b) by a variety of Lewis and Brønsted acids have been carried out at ambient temperature in dilute solution. With sulfuric acid in acetic anhydride 1a gives 3,5-di-*t*-butyl-4-acetoxybenzyl acetate (2) in excellent yield, whereas the major product resulting from the reaction of 1a with boron trifluoride etherate in benzene is 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (7). Evidence is presented for the intermediacy of quinone methide 3 in these reactions. In contrast, decomposition of 1a with hydrogen chloride in benzene gives mostly 2-*t*-butyl-6-chloro-*p*-cresol (20). Approximately 90% of 20 is formed by a mechanism that does not require the presence of a chlorinating agent which is able to attack aromatic nuclei. The remaining 10% of 20 results from chloroalkylation of 2,6-di-*t*-butyl-*p*-cresol (10) by a chlorinating species generated *in situ* from hydrogen chloride and *t*-butyl hydroperoxide. Hydrogen chloride catalyzed conversion of chlorodienone 22 to 20 occurs in high yield and proceeds by a mechanism which is entirely different from that involved in the hydrogen halide catalyzed conversion of bromodienone 23 to 2-*t*-butyl-6-bromo-*p*-cresol (24). Decomposition of 1b gave high yields of 2,6-di-*t*-butylquinone (8) under all of the conditions studied.

It is now generally agreed that inhibition of the low-temperature liquid phase autoxidation of hydrocarbons by hindered phenols² involves the formation of peroxy-cyclohexadienones.³ Mechanistic studies of inhibited autoxidation have frequently been carried out on the assumption that these peroxides were stable under the reaction conditions, and there seems to be no reason to doubt the validity of this postulate in most of the cases where it has been put forth. On the other hand, it is clear that there are many systems encountered in practical stabilization work where reactions of peroxy-cyclohexadienones are likely to occur.⁴ Drastic changes in over-all inhibition mech-

anisms might easily come about as a consequence of these reactions, and for this reason the chemistry of peroxy-cyclohexadienones is of potential practical interest.

The present paper is concerned with the acid-catalyzed⁵ decompositions of these peroxides, a topic which heretofore has not been subjected to systematic scrutiny. Two representative compounds, 1a and b, were selected for study, and the objectives of the work were twofold: first, to determine what products are formed from these substances when they are decom-



1a, R = CH₃
b, R = (CH₃)₃C

posed by common Lewis and Brønsted acids; and second, to arrive at qualitative descriptions of the

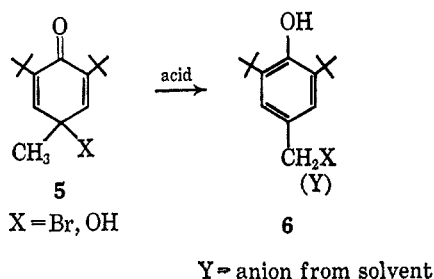
(1) Presented at the Southeast-Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 2, 1965. This paper constitutes part III of a series on oxidation inhibitors. Parts I and II are (a) N. P. Neureiter and D. E. Bown, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 236 (1962); (b) N. P. Neureiter, *J. Org. Chem.*, **28**, 3486 (1963).

(2) The literature through 1960 relating to this subject has been reviewed by K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).

(3) For examples of the preparation of alkylperoxy-cyclohexadienones and discussions of their role in inhibition, see (a) T. W. Campbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **74**, 1469 (1952); (b) A. F. Bickel, E. C. Kooyman, and C. la Lau, *J. Chem. Soc.*, 3211 (1953); (c) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 (1955); (d) E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 263,269 (1966).

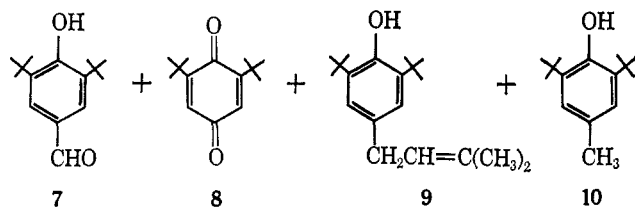
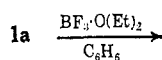
(4) See ref 1a for a discussion of some systems of this type.

(5) The term "acid-catalyzed" is used here merely for convenience, since there is no guarantee that all of the acids employed in this work functioned as true catalysts (*i.e.*, were not destroyed during reaction).



such intermediates, but which are all easily explicable in terms of a common mechanism involving addition of HX (or HY) to **3** in the characteristic 1,6 manner.¹³ In view of these facts and analogies, the quinone methide mechanism clearly seems to provide the best explanation for the formation of **2** in the peroxydienone reaction.¹⁴

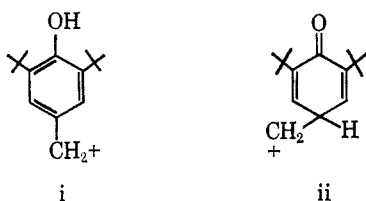
Decomposition of 1a with Boron Trifluoride Etherate in Benzene.—Experiment 2 gave a complex mixture of products whose identifiable constituents had the structures shown. The only one of these substances



not previously described in the literature was **9**, whose structure was verified by comparisons with an authentic sample prepared by alkylation of sodium 2,6-di-*t*-butylphenoxide with 1-bromo-3-methylbut-2-ene in dimethylformamide solution. Reaction of **3** with methylmagnesium chloride gave the isomeric alkenyl-

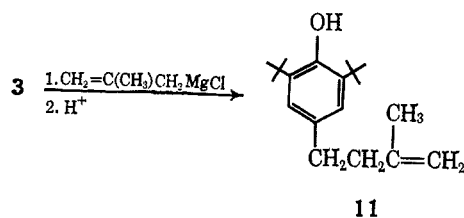
(13) (a) The 1,6 mode of addition to quinone methides is well documented; see A. B. Turner, *Quart. Rev.* (London), **18**, 347 (1964), and references therein. (b) Quinone methides have apparently not been observed directly in reactions of **5** and related substances, although the possibility of their formation in such reactions has been considered by numerous workers; cf. V. V. Ershov, A. A. Volod'kin, and G. N. Bogdanov, *Russ. Chem. Rev.*, **32**, 75 (1963), and literature cited therein.

(14) It might be argued that activation of the 4-methyl group of **1a** results from direct rearrangement of ion **18** to ion i (cf. ref 7, p 71) or to ion ii

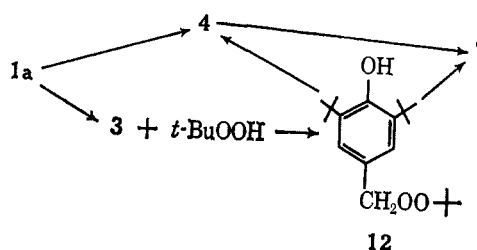


without intervention of **3**. However, the former process is extremely improbable for stereochemical reasons, and the latter one is also quite unreasonable, since it produces a primary ion in which the charge is not dispersed by conjugation. Although the carbonyl group undoubtedly destabilizes ion **18** to some degree, the fact that halodienones **22** and **23** are readily converted to the corresponding methoxydienone under conditions which are clearly indicative of S_N1 processes (see Experimental Section and ref 12a) strongly suggests that **18** is considerably more stable than ii, since simple primary alkyl halides are solvolyzed quite slowly under these conditions. Benzyl carbonium ions may well be intermediates in certain reactions of **1a**, but formation of such ions by processes which do not involve **3** is unlikely.

phenol, **11**, which could not be detected among the decomposition products of the peroxydienone.



As was the case with expt 1, the most interesting aspect of the reaction now under discussion is the functionalization of the 4-methyl group of **1a**. Several mechanistic paths leading to the major product, aldehyde **7**, were considered. One scheme involves direct



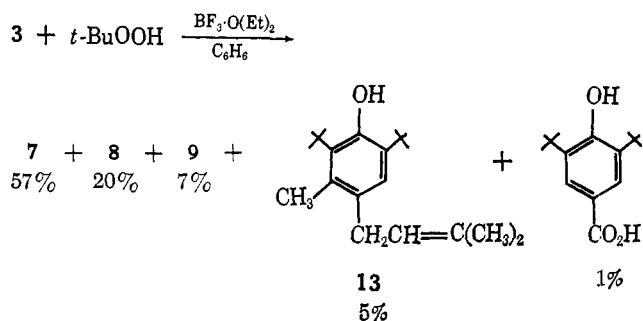
formation of **4** (see above), followed by rearrangement of this intermediate to the aldehyde. Such a rearrangement finds analogy in the reported conversion of certain spirooxiranes of this type to the corresponding *p*-hydroxybenzaldehydes upon treatment with boron trifluoride etherate under our conditions.^{5b,15} The key intermediate in the alternative routes leading to **7** is quinone methide **3**. Reaction of **3** with *t*-butyl hydroperoxide formed in the initial elimination step (or, alternatively, with hydrogen peroxide resulting from acid-catalyzed decomposition of this hydroperoxide) could give a benzyl peroxide,^{13a} **12** (or the corresponding hydroperoxide), whose acid-catalyzed decomposition might either lead to **4** or give **7** directly.¹⁶

For the reasons discussed earlier, the most probable mode of reaction of **1a** was considered *a priori* to be that which produces the quinone methide, and the formation of this intermediate in the present system is suggested by several lines of evidence. The first of these is the presence of alkenylphenol **9**, a product whose formation can be readily accounted for by a mechanism involving acid-catalyzed alkylation of isobutene (from the *t*-butylperoxy fragment) by the quinone methide. Secondly, reaction of the quinone methide with *t*-butyl hydroperoxide in the presence of boron trifluoride etherate gave a mixture of products which closely resembled the mixture formed from **1a** under comparable conditions.¹⁷

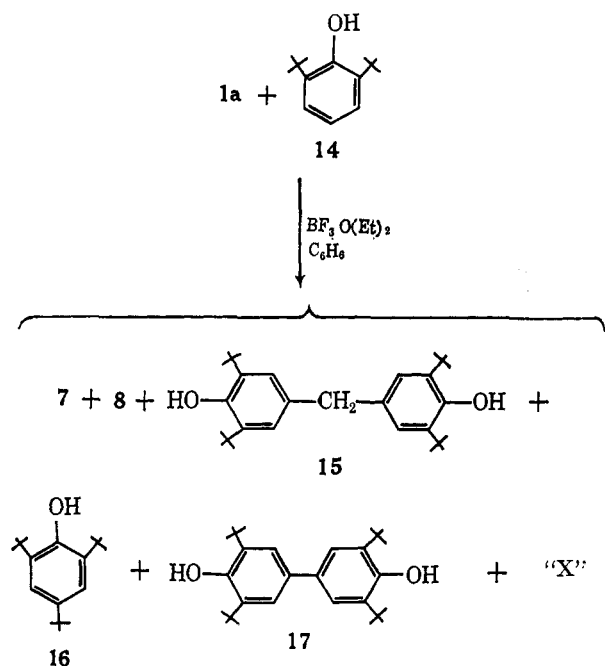
(15) In this connection, it is also of interest to note the reported conversion of **8** to **7** by reaction with diazomethane in methanol, a process which was suggested to involve **4** as an intermediate [W. Rundel and P. Kästner, *Tetrahedron Letters*, 3947 (1965)].

(16) The acid-catalyzed decomposition of **12** should resemble that of *p*-methylbenzyl hydroperoxide, which gives both *p*-tolualdehyde and *p*-cresol [cf. W. J. Farrissey, Jr., *J. Am. Chem. Soc.*, **84**, 1002 (1962), and references therein]. However, in the case of **12** the bridged ion responsible for carbon-to-oxygen aryl migration would be expected to lose a proton and form **4** as a stable intermediate.

(17) The origin of the 3-methyl group of **13** is obscure, and at present we have no evidence relating to this question. A small amount of **13** also may



Further evidence for the formation of **3** in the boron trifluoride etherate catalyzed decomposition of **1a** was obtained by carrying out the reaction in the presence of 2,6-di-*t*-butylphenol (**14**). Here it was anticipated that the presence of the quinone methide would be manifested by the formation of methylenebisphenol **15**, a compound which was produced in excellent yield when the reaction of **3** with **14** was carried out in a separate experiment. In fact, decomposition of **1a** with boron trifluoride etherate in the presence of 2 *M* equiv of **14** (expt 3) did give **15** as a major product. Significantly, aldehyde **7** was almost completely ab-

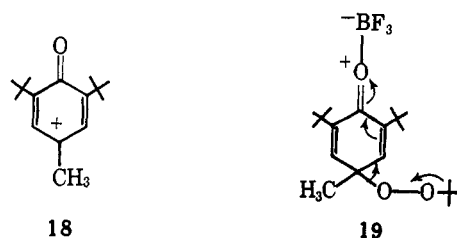


sent, and the remaining products consisted primarily of **8**, **16**, **17**, and a mixture, "X," which appeared as a single peak in the gas chromatogram. Compound **16** obviously results from alkylation of **14** by a species derived from the *t*-butylperoxy group, while the formation of **17** can only be accounted for by coupling of a pair of aryloxy radicals derived from **14**. The mechanism of formation of these radicals is unclear, and the possibility that they were produced in a trivial way, *viz.*, by air oxidation during the work-up, cannot be discounted.

Although "X" resisted complete characterization, its gas chromatographic retention time and mass spectrum strongly suggested that it was formed by re-

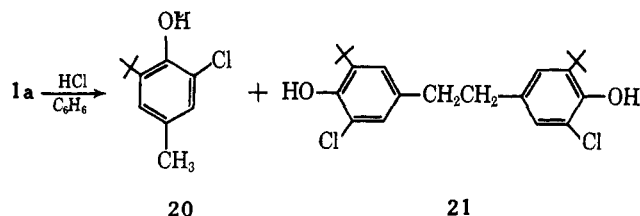
have been formed in the peroxydienone decomposition, but in this case the chromatographic peak corresponding to the compound was contaminated with other materials (see Experimental Section).

actions involving one molecule of the peroxydienone and one of **14**. Increasing the ratio of **14** to **1a** caused an increase in the yield of "X," and model experiments (see Experimental Section for details) showed that "X" was not formed from **15**, **7**, or **3**. These observations suggest that "X" resulted from entrapment by **14** of an intermediate (*e.g.*, ion **18**) which was also the precursor of **3**.¹⁸ It appears, therefore, that



10 is the only product of the peroxydienone decomposition (in the absence of **14**) which is necessarily formed by a mechanism that does not involve the quinone methide. The actual mode of formation of **10** is not clear; one possibility is concerted decomposition *via* **19**.

Decomposition of 1a with Hydrogen Chloride in Benzene.—In striking contrast to its decomposition behavior under other conditions, when **1a** was allowed to stand in benzene saturated with gaseous hydrogen chloride (expt 4), it afforded an excellent yield of chlorophenol **20**, together with a small amount of a material which was assigned structure **21** on the basis of high resolution mass spectral data and mechanistic considerations (see below). The structure of **20** was verified

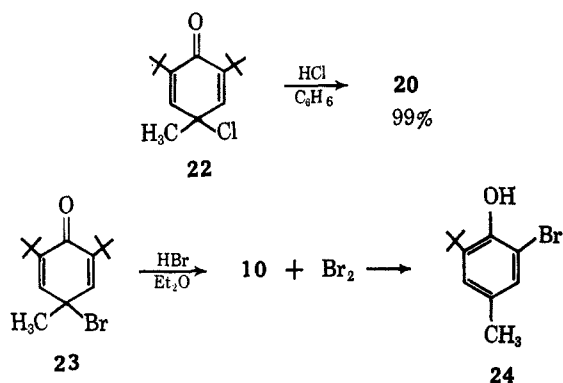


by analysis and the usual variety of spectroscopic measurements, as well as by an independent synthesis involving chlorination of 2-*t*-butyl-*p*-cresol with sulfuryl chloride.

In attempting to formulate a mechanism for the conversion of **1a** to **20**, we considered first the possibility that chlorodienone **22** was involved as an intermediate. Russian workers¹⁹ have reported that the corresponding bromodienone **23** reacts rapidly with excess hydrogen bromide in ether solution to form **10** and bromine; this transformation is then followed by slower processes, one of which gives bromophenol **24**. Moreover, the reaction of hydrogen chloride with bromodienones like **23** is said to proceed in similar fashion, except that in this case chlorine bromide is apparently the brominating agent formed *in situ*.¹⁹ In order to determine whether an analogous sequence of reactions might have

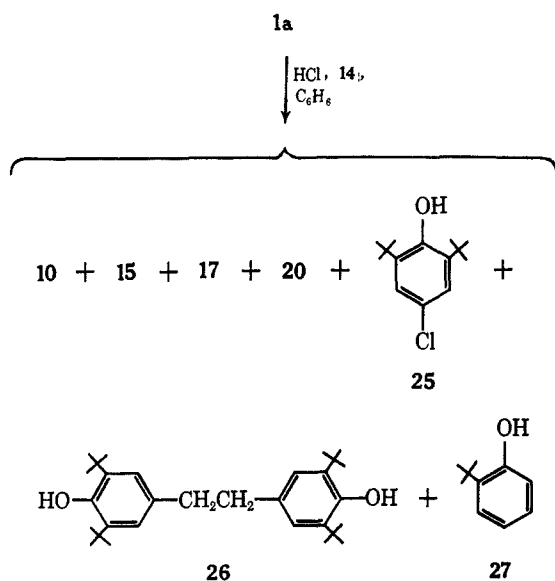
(18) It might be argued that the presence of **14** causes the decomposition to follow an entirely new course which leads directly to "X" and does not involve **3**. However, it does not seem likely that drastic alterations in the nature of the catalytic system would occur owing to interaction of boron trifluoride with **14**, since this highly hindered phenol should not be a particularly strong Lewis base.

(19) V. V. Ershov and A. A. Volod'kin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1935 (1962).



occurred in the peroxydienone system, separate experiments were carried out starting with 22. When this dienone was subjected to the action of hydrogen chloride in benzene, the result was virtually identical with that observed in the peroxydienone reaction, in that chlorophenol 20 was formed in nearly quantitative yield. However, a striking difference between halodienones 22 and 23 emerged when the reaction of 22 with hydrogen chloride was carried out in the presence of excess 14 (10 moles/mole of 22). This experiment yielded no trace of chlorinated products derived from the added phenol. Chlorophenol 20 was once again the major product (89% yield), and 11% of 15 (evidently derived from 3) was also detected. Since chlorination of 14 would certainly be expected if the chlorodienone had undergone initial conversion into chlorine and 10, it seems certain that the reaction of 22 with hydrogen chloride proceeds by a mechanism which is entirely different from that which operates in the reaction of bromodienone 23 with hydrogen halides.

Further peroxydienone decompositions performed in the presence of 14 (expt 5-6) furnished information which was particularly revealing. The results of these experiments indicate that a minor fraction of the decomposition leads to 3, since the presence of this in-



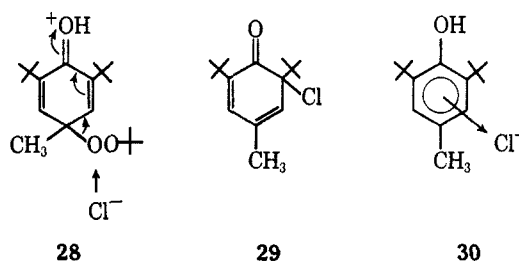
termediate seems to be necessary to account for the formation of bisphenols 15 and 26. Spontaneous dimerization of 3 probably produces a bisaryloxy radical;^{1b,20} this species could then react with 14 to

(20) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1201 (1963).

form 26 and two 2,6-di-*t*-butylphenoxy radicals, whose coupling would account for the production of bisphenol 17. The data suggest that there may be an additional mechanism for producing 2,6-di-*t*-butylphenoxy (for one possibility, see above), since the yield of 17 is greater than the yield of 26, and that the presence of 14 slightly increases the amount of decomposition *via* 3; however, these conclusions cannot be regarded as firm because of analytical uncertainties. The absence of fraction "X" (*cf.* preceding section) may be due to rapid deprotonation of 18 by chloride ion, or to direct formation of 3 in the present system by a concerted elimination process. Compound 27 obviously results from protodealkylation of 14.

Further consideration of the results of expt 4-6 strongly suggests that *two* mechanisms are operative in the conversion of 1a to 20. One mechanism involves the intermediate formation of 10 and its subsequent reaction with a chlorinating agent generated *in situ*.²¹ In the presence of 14 the chlorinating agent is scavenged (with formation of chlorophenol 25), and the yield of 10 obtained under these conditions provides a measure of the amount of 20 formed *via* 10 when 14 is absent. It should also be noted that chlorodealkylation of bisphenol 26 accounts for the formation of 21 rather than 26 when 14 is not present.

The generation of a chlorinating species in this system was of considerable interest, and neither the nature of this species nor its mode of formation was obvious *a priori*. In view of the experiments with chlorodienone 21 described above, it is certain that this compound is neither the chlorinating agent nor its precursor. An alternative possibility, which would also account for the formation of 10, is that a portion of the decomposition proceeds *via* 28 to produce *t*-BuOOCl, a species whose behavior as a chlorinating agent might be ex-



pected to resemble that exhibited by *t*-butyl hypochlorite.^{22a} However, the mechanism of formation of 10 remains uncertain (see the preceding section for another possibility), and, even if the speculative process leading to *t*-BuOOCl does occur, it fails to account for the fact that the yield of chlorophenol 25 is appreciably greater than the yield of 10. Another process which produces a chlorinating agent must occur in the system, and examination of the available facts suggests only one other reasonable contingency, *viz.*, that such an agent results from the reaction of hydrogen

(21) Aromatic substitutions involving replacement of *t*-butyl groups by chlorine are well known. For an example in the phenol series, see L. E. Forman and W. C. Sears, *J. Am. Chem. Soc.*, **76**, 4977 (1954).

(22) (a) *t*-Butyl hypochlorite reacts with 10 to give chlorodienone 29 [L. Denivelle and M. Hedayatullah, *Compt. Rend.*, **253**, 2711 (1961)], whose acid-catalyzed conversion to 20 should proceed with ease. (b) Facile loss of a *t*-butyl substituent from the quaternary ring carbon atom of cyclohexadienones has been observed by numerous workers. For some examples, see H. E. Albert and W. C. Sears, *J. Am. Chem. Soc.*, **76**, 4979 (1954); A. Rieker, *Ber.*, **98**, 715 (1965); and B. Miller and H. Margulies, *Tetrahedron Letters*, 1727 (1965).

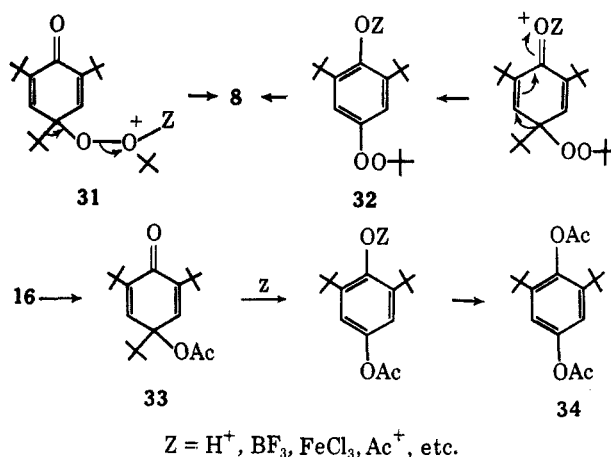
chloride with *t*-butyl hydroperoxide derived from the *t*-butylperoxy group of the peroxydienone. Although the ability of organic hydroperoxides to oxidize hydrogen iodide to iodine was axiomatic, to our knowledge there had been no demonstration that hydrogen chloride could be oxidized in a similar way, at least not at a useful rate.²³ However, when a solution of *t*-butyl hydroperoxide and **14** in benzene was allowed to react with hydrogen chloride under the conditions employed for the decomposition of **1a**, chlorophenol **25** was formed in 59% yield.²⁴ Moreover, in a similar experiment starting with equimolar amounts of **10**, **14**, and *t*-butyl hydroperoxide, chlorophenols **20** and **25** were produced in yields of 20 and 31%, respectively. These results provide strong confirmation for our suggested intermolecular chlorination route to **20** in the peroxydienone reaction, as well as an experimental demonstration of a chlorination technique which is believed to be novel and may prove to have synthetic utility. The chlorinating species is presumed to be chlorine (or Cl⁺), but hypochlorous acid and/or *t*-butyl hypochlorite may also be involved.

We are now left with the question of the route from **1a** to **20** which does not proceed by way of **10**. All of the data are consistent with the idea that this route involves chlorodienone **22** as a reactive intermediate, but alternative mechanisms involving allylic displacement (either stepwise or concerted) of the protonated *t*-butylperoxy group by chloride ion cannot be excluded. Such displacement would produce chlorodienone **29**, whose acid-catalyzed dealkylation should be rapid and quantitative.^{22b} A particularly intriguing mechanistic possibility is that chlorodienone **22** undergoes acid-catalyzed rearrangement to a chloronium π complex, **30** (which could either give **29** or form **20** directly), and this question is now under active investigation.

Decomposition of 1a with Other Acids.—Peroxydienone **1a** was slowly decomposed by sulfuric acid in benzene (expt 7) to give a material tentatively identified as **10** on the basis of nmr data. Reaction of **1a** with anhydrous ferric chloride in benzene gave a mixture which has not yet been characterized. No decomposition of the peroxydienone occurred when it was allowed to stand for several days with an equimolar amount of trifluoroacetic acid in benzene, or with sulfuric acid in *t*-butyl alcohol solution.

Acid-Catalyzed Decompositions of 1b.—The mode of decomposition of **1b** is apparently controlled by the thermodynamic stability of the incipient carbonium ion derived from the 4-*t*-butyl group. Under all

conditions studied, the major product was quinone **8**, whose formation could result either from direct decomposition of **31**, or from a multistep process involving peroxide **32** as an intermediate.^{22b}



Conversion of this peroxide to **8** might be accomplished by acid-catalyzed 1,6 elimination of *t*-BuOZ or, if Z is hydrogen, by a mechanism involving spontaneous homolysis of the oxygen-oxygen bond²⁵ followed by rapid disproportionation of the resulting aryloxy and *t*-butoxy radicals. In only one case (expt 8) were by-products observed; all of these were not identified, although diacetate **34** was shown to be their principal constituent. None of the by-products was formed from the quinone, since this material was shown to be inert under the experimental conditions. A possible route to **34** involves loss of *t*-butyl from acetoxydienone **33**,^{22b} but other mechanisms involving the hypothetical intermediate **32** can also be visualized.

Finally, it is of interest to recall here the suggestion of Hammond, *et al.*,²⁶ that 4-peroxy-2,5-cyclohexadien-1-ones derived from phenol (unsubstituted) might be converted to *p*-benzoquinone by reaction with ferric chloride. Our result with **1b** shows that this type of reaction can occur if the nonperoxidic 4 substituent is sufficiently labile.

Experimental Section²⁷

Materials.—*t*-Butyl hydroperoxide (Wallace and Tiernan, nominal purity 90%) was either used as received or purified by distillation (all-glass apparatus) at reduced pressure; the peroxide content was determined by iodometry. Benzene (reagent grade) was dried over sodium wire. Literature procedures

(23) Oxidation of chloride ion by hydrogen peroxide has been reported, but the rate of this reaction is only about 10⁻⁶ times the rate of oxidation of iodide ion under comparable conditions (aqueous solution, 25°). See J. O. Edwards, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p 67 ff, and references therein.

(24) On the assumption of second-order kinetics (first order in each reactant) for the oxidation of hydrogen chloride by *t*-butyl hydroperoxide, it is possible to estimate a *minimum* value of the rate constant for this process. Taking the yield of **25** as the measure of the rate, and using 0.343 moles l.⁻¹ as the concentration of hydrogen chloride [calculated from the appropriate Bunsen coefficient (Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," Band II, Teil 2b, Springer-Verlag, Berlin, Germany, 1962, p 1-80), correcting for the vapor pressure of benzene at 25° ("International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 221)], the value obtained is 7 × 10⁻⁶ l. mole⁻¹ sec⁻¹. Although this value is about 64 times larger than the rate constant for oxidation of chloride ion by hydrogen peroxide in water at 25° (ref 23, p 79), it does not necessarily indicate that the present reaction is *abnormally* fast, since oxidations of this kind are known to be strongly catalyzed by acids.²³

(25) The thermal instability of aryl peroxides is well documented; *cf.* C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6032 (1955); H. Hoek and F. Ernst, *Ber.*, **92**, 2732 (1959); W. E. Lee, J. G. Calvert, and E. W. Malmberg, *J. Am. Chem. Soc.*, **83**, 1928 (1961).

(26) G. S. Hammond, L. R. Mahoney, and U. S. Nandi, *ibid.*, **85**, 737 (1963).

(27) Melting points and boiling points are uncorrected. Melting points were determined with a Fisher-Johns apparatus, except where noted differently. Distillations were performed with a spinning-band column (18 in. × 6 mm) unless noted otherwise. Evaporations were carried out with a Rinco rotary evaporator at ambient temperature and 5-10-mm pressure. Organic liquids were dried over Drierite. Reactions performed under the "usual" conditions were carried out in the dark under nitrogen at ambient temperature. Mixtures worked up in the "usual" way were processed according to the procedures employed for peroxydienone decompositions carried out in the same solvents (see text). Elemental microanalyses were done by Schwarskopf Microanalytical Laboratory, Woodside, N. Y., unless otherwise noted. Miss T. Reid and Messrs. T. J. Denson, J. Dzilsky, T. Hines, H. W. Kinsey, V. H. Rushing, G. R. Taylor, and J. L. Taylor performed various instrumental analyses.

were used to prepare reference samples of 7,²⁸ 8,²⁹ 3,5-di-*t*-butyl-4-hydroxybenzoic acid,³⁰ and 26.³¹ All other chemicals used were commercial products, purified (if necessary) by conventional methods until their physical constants agreed with literature values.

Instrumental Analyses.—Infrared spectra were recorded with a Perkin-Elmer instrument, Model 21. Nmr spectra were obtained with a Varian A-60 instrument using dilute solutions containing tetramethylsilane for internal standardization. Low-resolution mass spectra were obtained with a CEC instrument, Type 21-103C; the high-resolution measurements were made with an AEI MS-9 spectrometer and are referred to $C = 12 \mu$ as standard. Ultraviolet spectra were obtained with a Cary recording spectrophotometer, Model 14. Analyses by programmed temperature gas chromatography were done with an F & M instrument, Model 500, using the following columns: A, 15% XE-60 on 40–60 mesh Chromosorb P (10 ft \times 0.25 in.); B, 15% SE-30 on 45–60 mesh Chromosorb W (6 ft \times 0.25 in.); C, 0.5% SE-30 on 45–60 mesh Chromosorb W (6 ft \times 0.25 in.); D, 15% SE-30 on 45–60 mesh Chromosorb P (6 ft \times 0.25 in.). Column temperature was increased from approximately 100 to 350° at the rate of 8°/min; helium was used as the carrier gas. All constituents of mixtures were assumed to have equal gas chromatographic sensitivity factors; trapped fractions were identified by a combination of infrared, nmr, and mass spectral techniques.

Preparation of Peroxycyclohexadienones 1a and b.—These compounds were obtained by reaction of phenol 10 or 16 with *t*-butyl hydroperoxide in the presence of cobalt naphthenate according to a published procedure.^{3b}

Recrystallization of crude 1a from methanol gave snow white needles, mp 85.5–86.5° (lit.^{3b} mp 87°). The nmr spectrum (CCl_4) of this material showed sharp singlets at τ 3.53, 8.71, 8.77, and 8.81, corresponding to the olefinic protons, the 4-methyl group, the *t*-butyl substituents in the 2 and 6 positions, and the *t*-butylperoxy group, respectively. The resonances at τ 8.71–8.81 were not sufficiently resolved to permit their separate integration, although their intensities were qualitatively in accord with the expected values. The ratio of the total area of the τ 8.71–8.81 group to that of the τ 3.53 peak was 30:2.

Difficulties were encountered in purifying 1b according to the published method;^{3b} however, material of excellent purity was readily obtained by a chromatographic technique. In a typical experiment, the crude product (35.0 g) obtained from the reaction of 26.2 g (0.100 mole) of phenol 16, 20.0 g (0.211 mole) of 95.0% *t*-butyl hydroperoxide, and 2.63 g of cobalt naphthenate (6% nominal cobalt content) in 100 ml of dry benzene was chromatographed on 500 g of alumina (Merck reagent) wetted with petroleum ether (bp 30–60°), using petroleum ether for elution, with the following results (fraction number, volume of eluate, weight of residue left after evaporation of solvent, description of residue): 1, 250 ml, 0.16 g, water white liquid; 2, 50 ml, 2.35 g, pale yellow viscous liquid; 3, 300 ml, 21.71 g, pale yellow viscous liquid; 4, 880 ml, 5.15 g, pale yellow viscous liquid. Fraction 1 was not identified. Fraction 3 solidified upon refrigeration and was found (bulb immersion thermometer) to remelt at $\sim 9^\circ$ (for 1b, lit.^{3b} mp 5°). The infrared spectrum (neat sample) of this fraction showed no OH absorption but did display a strong doublet at 1681–1658 cm^{-1} which was indicative of the cross-conjugated dienone structure (compare the reported spectrum^{3a} of 1a). The nmr spectrum ($CDCl_3$) consisted of sharp singlets at τ 3.33 (2 H, olefinic hydrogens) and 9.03 (9 H, 4-*t*-butyl group), together with two sharp, incompletely resolved peaks (27 H) at 8.75 (2- and 6-*t*-butyls) and 9.03 (*t*-butylperoxy group) whose separate intensities were qualitatively in accord with the assignments given. Maxima appeared in the ultraviolet spectrum (isooctane) at 237 $m\mu$ ($\log \epsilon$ 4.08) and 372 $m\mu$ ($\log \epsilon$ 1.46), but there was no trace of a maximum or shoulder in the 300–320- $m\mu$ region. (The sample of 1b prepared by Bickel, *et al.*,^{3b} showed a maximum at 317 $m\mu$ which these workers ascribed to an impurity, a conclusion now shown to be correct.) These data show that fraction 3 was pure 1b (62% yield), uncontaminated by the isomeric 2,4-dienone.

*Anal.*³² Calcd for $C_{22}H_{32}O_2$: O, 13.69. Found: O, 13.83.

(28) T. H. Coffield, A. H. Filbey, G. G. Ecke, and A. J. Kolka, *J. Am. Chem. Soc.*, **79**, 5019 (1957).

(29) K. Ley and E. Müller, *Ber.*, **89**, 1402 (1956).

(30) E. Müller, A. Rieker, R. Mayer, and K. Scheffler, *Ann.*, **645**, 36 (1961).

(31) C. R. Bohn and T. W. Campbell, *J. Org. Chem.*, **22**, 458 (1957).

Fractions 2 and 4 were shown by nmr analysis to consist largely of 1b, but attempts to recover the pure material from these fractions were not made.

Samples of 1a and b showed no signs of deterioration after having been stored at -20° in the dark for more than a year, as was evidenced by nmr spectral comparisons.

Acid-Catalyzed Decompositions of 1a and b. A. General Comments.—Solutions of the peroxides in the appropriate solvents were prepared immediately before use and were stirred rapidly under nitrogen while the desired amounts of acidic reagents (either pure or dissolved in small quantities of solvent) were added dropwise during 2–5 min. The reaction vessels were then filled with nitrogen, stoppered tightly, and allowed to stand at ambient temperature in the dark for the desired periods of time. Mixtures containing acetic anhydride were added cautiously to ice water (*ca.* 3 ml/ml of Ac_2O) and allowed to stand in the refrigerator until hydrolysis was complete. Products were recovered by extracting two or three times with ether, and acetic acid was removed from the combined extracts (total volume approximately equal to that of the mixture after hydrolysis) by washing with portions of 3 *N* sodium carbonate until a strongly basic aqueous layer was obtained. The organic layer was then washed with one-half its volume of saturated sodium chloride solution, dried, and evaporated to give a solvent-free residue which was subjected to analysis. For experiments using benzene as solvent, reaction mixtures were extracted with 1 or 3 *N* aqueous sodium carbonate (occasionally after a preliminary washing with water) until a basic extract was obtained. The combined aqueous phases were back-extracted with small portions of ether until clear, warmed to expel ether, acidified (pH 2) with concentrated hydrochloric acid, and chilled; however, no acids precipitated from these solutions in any of the experiments. The combined organic phases were worked up in the manner described above, except that the washing with sodium chloride solution was usually eliminated. Procedural and analytical details for individual experiments are given below.

B. Compound 1a with Sulfuric Acid in Acetic Anhydride.—The crude product, a pale yellow oil, gave an infrared spectrum (neat) which was identical with that of authentic 2 except for a very weak impurity band at 856 cm^{-1} . Distillation at reduced pressure gave a sample whose infrared and nmr spectra were identical in every respect with those of the pure material. The yield of 2 reported for expt 1 is based on the weight of product prior to distillation.

C. Compound 1a with Boron Trifluoride Etherate in Benzene.—Gas chromatographic analysis (column A) of the product from expt 2 showed seven principal peaks, comprising 85% of the total area, and a number of smaller peaks, none of which amounted to more than 2–3 area %. The principal peaks were trapped separately and examined spectroscopically. Peaks 2, 3, and 7 (numbers refer to order of elution) were shown to correspond to compounds 10, 8, and 7, respectively, by comparing their retention times and various spectral properties with those of authentic specimens. Peak 1 (4 area %) showed low-resolution mass spectral peaks (70 *v*) at *m/e* 218 (medium) and *m/e* 203 (strong) and, therefore, may have contained quinone methide 3; however, the fact that the spectrum gave no evidence for the presence of dimeric products³⁰ derived from 3 tends to militate against its presence. Further examination of peak 1 was not undertaken because of the small amount of material on hand. Mass and infrared spectra and the retention time of peak 5 showed that it consisted of 9 and lesser amounts of other materials; the yield reported for 9 is based on an assumed purity of 100% for peak 5 and is probably high by 1–4%. Peak 4 (4 area %) and peak 6 (9 area %) could not be characterized and appeared to be mixtures, although the retention time and low resolution mass spectrum of peak 4 suggested that one of its components was 13. The relative amounts of 7, 8, and 10, determined by nmr analysis, were in satisfactory agreement with the values obtained by gas chromatography; however, the complexity of the product mixture precluded its complete analysis by the nmr technique.

Gas chromatographic analysis (column B) of the product from expt 3 gave the results reported in Table I and also showed that 34 area % (54% recovery) of 14, 6 area % of minor (unidenti-

(32) Neutron activation analysis was performed under the direction of Dr. R. L. Hull.

fied) constituents, and 18 area % (0.65 times area of peak corresponding to 15) of the fraction designated as "X" were present. Products were identified in the usual way by comparisons (retention times, spectra of trapped fractions) with authentic samples. The infrared spectrum (CS_2) of "X" exhibited a strong, sharp band at 3620 cm^{-1} (OH of hindered phenol) and absorption of medium intensity, presumably due to conjugated carbonyl (cyclohexadienone?), at 1650 and 1638 cm^{-1} (exact position of last band doubtful because of interference by solvent). The nmr spectrum (CS_2) was not particularly informative; it suggested that "X" was a complex mixture and consisted of several weak peaks at τ 2.5–3.6 for aromatic and olefinic (cyclohexadienone?) hydrogens, a number of weak peaks at τ 4.8–5.2 (hindered phenolic OH), and several peaks of varying intensity at τ 8.0–9.15 (aliphatic protons). The high-resolution mass spectrum (12 v) showed peaks at m/e 310.1933 (calcd for $\text{C}_{21}\text{H}_{26}\text{O}_2$: 310.1936), m/e 312.2089 (calcd for $\text{C}_{21}\text{H}_{28}\text{O}_2$: 312.2090), m/e 366.2559 (calcd for $\text{C}_{25}\text{H}_{34}\text{O}_2$: 366.2555), m/e 368.2715 (calcd for $\text{C}_{25}\text{H}_{36}\text{O}_2$: 368.2709), and m/e 422.3185 (calcd for $\text{C}_{25}\text{H}_{42}\text{O}_2$: 422.3175), whose relative intensities were 1.0, 3.8, 3.4, 7.0, and 10.2, respectively. A separate experiment starting with 75 $\mu\text{moles/l.}$ of 1a and 750 $\mu\text{moles/l.}$ of 14 gave similar results; however, in this case aldehyde 7 was completely absent, and the area of the peak corresponding to "X" was 1.75 times the area of the peak corresponding to 15. The following experiments argue against formation of "X" from 15 or from 7; part D of "Reactions of 3" (below) argues against formation of "X" from 3.

Boron trifluoride etherate (0.85 g, 6.0 μmoles) was added to a solution of 14 (9.28 g, 45.0 μmoles), 15 (2.12 g, 5.0 μmoles), and *t*-butyl hydroperoxide (91.7% pure, 0.49 g, 5.0 μmoles) in 55 ml of dry benzene, and the mixture was worked up in the usual way after 24 hr of reaction under the usual conditions. Analysis of the carbonate-insoluble residue by gas chromatography (column B) showed that the only materials present were 14–16 (18% yield of 16, based on hydroperoxide).

A solution of 7 (0.59 g, 2.5 μmoles), 14 (10.25 g, 49.7 μmoles), and boron trifluoride etherate (0.85 g, 6.0 μmoles) in 55 ml of dry benzene underwent no detectable reaction (analysis by gas chromatography, column B) after 22 hr of standing under the usual conditions.

D. Compound 1a with Hydrogen Chloride in Benzene.—Mixtures produced in expt 4–6 were analyzed by gas chromatography using column B. All products except 21 were identified by comparing their retention times and the spectral properties of trapped peaks with those of pure compounds. A pure sample of 20, bp $105\text{--}106^\circ$ at 10 mm, was isolated by distillation of the product from a large-scale experiment similar to expt 4. This material showed a strong, sharp infrared band (neat sample) at 3510 cm^{-1} (hindered OH), and its nmr spectrum (CDCl_3) consisted of singlets at τ 8.61 (9 H, *t*-butyl group), 7.83 (3 H, 4-methyl group), 4.44 (1 H, hydroxyl), and 3.12 (2 H, ring protons, note accidental degeneracy). The mass spectrum exhibited parent peaks at m/e 198.0818 (calcd for $\text{C}_{11}\text{H}_{15}\text{Cl}^{35}\text{O}$: 198.0811) and m/e 200.0780 (calcd for $\text{C}_{11}\text{H}_{15}\text{Cl}^{37}\text{O}$: 200.0782) whose intensities at 12 v were in the expected ratio (3:1, respectively).

Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{ClO}$: C, 66.49; H, 7.61; Cl, 17.84. Found: C, 66.39; H, 7.48; Cl, 17.70.

The structure assigned to 21 is based on mechanistic analogies (see text) and the mass spectrum of a trapped fraction, which showed parent peaks at m/e 394.1465 (calcd for $\text{C}_{22}\text{H}_{28}\text{Cl}_2^{35}\text{O}_2$: 394.1464), m/e 396, and m/e 398, whose intensities at 12 v were in the ratio expected for a material containing two atoms of chlorine. Strong peaks also appeared in the spectrum (70 v) at m/e 197 and m/e 199 (presumably $\text{C}_{11}\text{H}_{14}\text{Cl}^{35}\text{O}$ and $\text{C}_{11}\text{H}_{14}\text{Cl}^{37}\text{O}$ resulting from breakage of the central C–C bond). The absence of the isomeric structure containing two *t*-butyls on one ring and two chlorine atoms on the other was inferred from the presence of only a very weak peak at m/e 175 ($\text{C}_7\text{H}_7\text{Cl}_2^{35}\text{O}$). However, the presence of relatively weak parent peaks at m/e 416 and 418 (intensity ratio at 12 v ca. 3:1, respectively), together with a strong peak at m/e 219 (70 v), suggested that a small amount of 1-(3-*t*-butyl-5-chloro-4-hydroxyphenyl)-2-(3,5-di-*t*-butyl-4-hydroxyphenyl)ethane was also present in the fraction containing 21. The yields reported for expt 5 and 6 are normalized values whose calculation involved setting the total of the yields of 10, 15, 20, and 26 equal to 100%. In these two experiments approximately 2% of the total gas chromatographic area consisted of minor, unidentified peaks, while in the

case of expt 4 the unidentified constituents amounted to about 6 area %.

E. Compound 1a with Sulfuric Acid in Benzene.—The results reported for expt 7 were obtained by nmr analysis. All of the peaks assigned to 10 were detectable, and their intensity ratios were in accord with the theoretical values.

F. Compound 1b with Sulfuric Acid in Acetic Anhydride.—Analysis by gas chromatography (column C) gave the results reported for expt 8. The identities of compounds 8 and 34 were confirmed by the usual variety of comparisons. Several small peaks, none of which amounted to more than 4 area %, were also detected. An experiment in which the reaction time was 26 hr gave 8 and 34 in yields that were the same (within experimental error) as those reported for expt 8.

A solution of 8 (0.55 g, 2.5 μmoles) and sulfuric acid (0.5 g) in acetic anhydride (32.5 ml) was allowed to stand under the usual conditions for 4 days and then worked up as usual. The quinone was recovered in quantitative yield and identified by nmr analysis.

G. Compound 1b with Boron Trifluoride Etherate in Benzene.—The crude product from expt 9 was shown to be essentially pure 8 by nmr analysis.

H. Compound 1b with Hydrogen Chloride in Benzene.—Analysis of the product from expt 10 by nmr showed that it consisted almost entirely of 8.

I. Compound 1b with Sulfuric Acid in Benzene.—Analysis by nmr showed that the product from expt 11 contained only 8 and unreacted 1b. The reported percentages are normalized.

J. Compound 1b with Ferric Chloride in Benzene.—The reaction mixture from expt 12 was mixed thoroughly with excess 3 *N* sodium carbonate, filtered, and then worked up in the usual way. The reported percentages of 1b and 8 were obtained by nmr analysis and are normalized.

Preparation of 4-Methylene-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one (3).—Chloromethylation of 14 according to Neureiter's procedure^{1b} gave a solution of 2,6-di-*t*-butyl-4-chloromethylphenol in *n*-heptane. Evaporation of the solution, followed by two crystallizations of the residue from petroleum ether (bp $30\text{--}60^\circ$, ca. 1 ml/g of product) at Dry Ice temperature, gave a pure product, mp $41\text{--}43^\circ$, which contained no impurities detectable by nmr analysis. Dehydrochlorination of solutions (approximately 10^{-3} M) of the chloromethylphenol in benzene with equivalent amounts of triethylamine^{1b} gave solutions of 3, which were filtered to remove triethylamine hydrochloride and used immediately after preparation. Conversions to 3 were essentially quantitative, since the yields of triethylamine hydrochloride (washed with fresh solvent, dried *in vacuo*) were always 99.8–100.0%.

Reactions of 3. A. With Sulfuric Acid and Acetic Anhydride.—A solution of 2.0 ml of concentrated sulfuric acid in 100 ml of acetic anhydride was chilled in an ice bath and stirred while a cold (ca. 10°) solution of 3 (25.5 μmoles) in 225 ml of dry benzene was added rapidly.³³ After 21 hr of standing under the usual reaction conditions, the benzene was evaporated, and the mixture was then processed according to the usual procedure for reactions carried out in acetic anhydride. The crude product (7.47 g) was a straw-colored liquid whose nmr spectrum showed that it consisted of 2 together with only small amounts of impurities. Distillation of a 6.93-g portion of the liquid gave only one fraction, a colorless, viscous oil that weighed 5.68 g (75% yield, corrected to total weight of crude product), had bp $126\text{--}127^\circ$ at 0.18–0.20 mm, and solidified into white crystals, mp $50\text{--}55^\circ$, upon scratching. The infrared spectrum (neat sample) showed no OH absorption but displayed strong carbonyl bands at 1757 and 1776 cm^{-1} . The nmr spectrum (CDCl_3) consisted of singlets at τ 2.67 (2 H, aromatic protons), 4.96 (2 H, methylene group), 7.72 (3 H, ring acetoxy), 7.98 (3 H, side chain acetoxy), and 8.62 (18 H, *t*-butyl groups) and remained unchanged upon addition of deuterated acetic acid. Redistillation afforded an analytical sample of 2, bp 127° at 0.20 mm.

Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_4$: C, 71.22; H, 8.81. Found: C, 71.49; H, 8.73.

B. With *t*-Butyl Hydroperoxide and Boron Trifluoride Etherate.—A solution of 3 (25.5 μmoles) in 280 ml of anhydrous benzene was combined with a solution of *t*-butyl hydroperoxide (95.0% pure, 2.42 g, 25.5 μmoles) in 50 ml of the dry solvent.

(33) Later experiments suggested that use of cold solutions was unnecessary.

Boron trifluoride etherate (4.30 g, 30.3 mmoles) was then added dropwise during 5 min while the mixture was stirred rapidly under nitrogen. Stirring in the inert atmosphere was continued for 10 min, during which time the initial mildly exothermic reaction gradually subsided. The reaction vessel was then stoppered and allowed to stand under the usual conditions for 24 hr. Work-up of the resulting reddish brown mixture was carried out in the usual way. Acidification of the basic aqueous extracts precipitated 0.07 g of solid which was shown by infrared and nmr analysis to be a 65:35 mixture of 3,5-di-*t*-butyl-4-hydroxybenzoic acid (1% yield, formed by oxidation of **7**) and aldehyde **7**, respectively. The gas chromatogram (column A) of the carbonate-insoluble residue (5.69 g) exhibited four principal peaks (94.5% of the total area), three of which were shown to be **7** (57% total yield), **8** (20% yield), and **9** (7% yield) by the usual comparisons (retention times, spectral properties of trapped fractions). The relative amounts of **7** and **8**, determined by nmr analysis, were in satisfactory agreement with the values obtained by gas chromatography. The fourth principal chromatographic peak showed infrared bands (CS_2) for hindered phenolic OH at 3650 cm^{-1} (sharp, strong intensity) and for trisubstituted olefin at 1667 (medium) and 810 cm^{-1} (medium). The mass spectrum (8 v) displayed a strong peak at m/e 288.2449 (calcd for $\text{C}_{20}\text{H}_{20}\text{O}$: 288.2453), while the spectrum at 70 v had peaks at m/e 288 and 233 of approximately equal (medium) intensity. A completely satisfactory nmr spectrum could not be obtained with the small amount of material on hand because of the low signal-to-noise ratio; however, the presence of two types of *t*-butyl groups was indicated by two sharp peaks of approximately equal intensity at τ 8.58 and 8.53. On the basis of these data structure **13** (5% yield) is assigned to the compound corresponding to the fourth chromatographic peak.

In a duplicate experiment, the carbonate-insoluble residue was triturated with cold (-20°) methanol and filtered to recover 3.77 g (63% yield) of **7**, mp $191.5\text{--}192.5^\circ$ (lit.^{2a,28} mp 189°).

C. With **14 and Boron Trifluoride Etherate.**—Boron trifluoride etherate (2.54 g, 17.9 mmoles) was added to a solution of **3** (15.0 mmoles) and **14** (6.19 g, 30.0 mmoles) in 190 ml of dry benzene, and the mixture was allowed to react under the usual conditions for 27.5 hr. Work-up by the usual procedure gave 9.83 g of carbonate-insoluble residue whose gas chromatogram (column D) exhibited two principal peaks. These were shown to be unreacted **14** (62% recovery) and bisphenol **15** (94% yield) by the usual variety of comparisons with pure reference compounds.

D. With **14, *t*-Butyl Hydroperoxide, and Boron Trifluoride Etherate.**—This reaction was carried out in the manner described in the preceding section using a solution of **3** (15.0 mmoles) in 140 ml of dry benzene, a solution of **14** (6.19 g, 30.0 mmoles) and *t*-butyl hydroperoxide (91.7% pure, 1.47 g, 15.0 mmoles) in 50 ml of the solvent, and 2.54 g (17.9 mmoles) of boron trifluoride etherate. After 27 hr of standing the mixture was worked up in the usual way. The basic extracts yielded 0.04 g of solid, mp $192\text{--}197^\circ$, which was shown to be mostly aldehyde **7** by nmr and infrared measurements. Trituration of the residue with 20 ml of methanol, followed by filtration, gave 1.63 g of **7**, mp $190\text{--}191^\circ$, whose infrared spectrum was essentially identical with that of the authentic material. The methanol extract was evaporated, and the residue (7.69 g) was analyzed by gas chromatography (column B). The five principal peaks (97% of the total area) were shown by the usual comparisons to be **14** (61% recovery), **7** (64% yield, including material recovered previously), **15** (19% yield), **16** (30% yield, based on hydroperoxide), and **17** (11% yield, based on **14**).³⁴

(34) The absence of alkenylphenols **9** and **13** from the products is understandable, since here the concentration of isobutene is greatly reduced by the competing alkylation reaction leading to **16**. A more puzzling feature is the absence of quinone **8**, an observation whose explanation must await definitive information as to the mechanism of formation of the quinone in this system when **14** is not present. The relative inefficiency of **14** as a trapping agent for the quinone methide under these conditions is apparently related to the relatively high initial concentration of hydroperoxide. In the peroxydienone decomposition, where trapping by **14** is more efficient, the hydroperoxide is formed slowly *in situ* and is kept from attaining a high concentration by its concurrent acid-catalyzed decomposition. The fraction of hydroperoxide which is destroyed by such decomposition should be greater in the peroxydienone reaction than in reactions starting with **3**, since in the former case the competing reaction of hydroperoxide with **3** would be disfavored by the relatively low steady-state concentration of the quinone methide.

Preparation of 2,6-Di-*t*-butyl-4-(3-methyl-2-buten-1-yl)phenol (9**).**—A solution of **14** (9.32 g, 45.2 mmoles) and sodium methoxide (2.70 g, 50.0 mmoles) in reagent grade methanol (50 ml) was evaporated to dryness *in vacuo*, and the residual salt was quickly dissolved in 50 ml of anhydrous dimethylformamide (dried by distillation from calcium hydride) under nitrogen. The solution was stirred while 1-bromo-3-methylbut-2-ene (7.45 g, 50.0 mmoles) was added dropwise over a 10-min period. During this addition the temperature rose to 51° , and a white solid (presumably sodium bromide) appeared. After having been stirred overnight at ambient temperature under nitrogen, the mixture was warmed at $91\text{--}97^\circ$ for 1 hr, cooled, diluted with 250 ml of water, and extracted with four 100-ml portions of ether. The combined extracts were washed in succession with three 100-ml portions of 10% hydrochloric acid and three 75-ml portions of 3 *N* sodium carbonate, dried, and evaporated. Distillation of the residue failed to give a satisfactory separation of products; however, a fraction with bp 164° at 10 mm was obtained which proved to be essentially pure **9**. The infrared spectrum (neat sample) of the material showed a strong, sharp band at 3630 cm^{-1} (hindered OH) and a rather broad band of medium intensity at 1665 cm^{-1} (trisubstituted olefin). Peaks appeared in the nmr spectrum (CDCl_3) at τ 8.60 (18 H, singlet, *t*-butyl groups), 8.29 (6 H, singlet, methyl groups attached to the double bond), 6.79 (2 H, doublet with $J = \sim 8$ cps, methylene group), 5.11 (1 H, singlet, hydroxyl proton), 4.73 (1 H, triplet with $J = \sim 8$ cps, vinyl proton), and 3.12 (2 H, singlet, ring hydrogens). The mass spectrum (70 v) showed a peak at m/e 219 whose intensity was about two-thirds that of the strong parent peak at m/e 274. An analytical sample of the compound was prepared by redistillation; the boiling point was identical with that of the material obtained previously.

Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}$: C, 83.15; H, 11.02; mol wt, 274.2296. Found: C, 83.54; H, 11.25; mol wt, 274.2298 (mass spectrum).

The nmr spectra of the lower boiling fractions (bp $115\text{--}152^\circ$ at 10 mm) obtained in the original distillation showed that they also contained considerable amounts of **9**, but further attempts to purify these fractions were not made.

Preparation of 2,6-Di-*t*-butyl-4-(3-methyl-3-buten-1-yl)phenol (11**).**—Following a procedure similar to that described in the literature,²⁸ a Grignard reagent was prepared from 3.41 g (37.7 mmoles) of methallyl chloride and 1.00 g (41.3 mg-atoms) of magnesium in 50 ml of dry ether containing a crystal of iodine. After approximately 8 hr of stirring at $0\text{--}7^\circ$ under nitrogen, the mixture was allowed to warm to 18.5° , and a freshly prepared solution of **3** (31.4 mmoles) in 340 ml of anhydrous benzene was added over a 20-min period. Stirring was continued for an additional 20 hr in a dry atmosphere at ambient temperature; then the red-violet solution was decanted from a considerable amount of unreacted magnesium and mixed thoroughly with 800 g of crushed ice in an excess of dilute hydrochloric acid. The cloudy aqueous layer was separated and extracted with 200 ml of ether, and the combined organic phases were washed with two 150-ml portions of 3 *N* sodium carbonate solution, dried, and evaporated. The red-brown semisolid residue (7.74 g) was triturated with 50 ml of petroleum ether (bp $30\text{--}60^\circ$) and filtered; the recovered material, an orange-red solid (1.64 g), melted at $250\text{--}292^\circ$ and was shown by nmr analysis to be a mixture of dimeric products derived from the quinone methide. An additional 0.12 g of dimeric materials precipitated when the solution was concentrated and chilled; this solid was separated, and the filtrate was then distilled to give 0.67 g (8% yield) of **11**, bp 125° at 2.2 mm, a yellowish oil that slowly solidified upon standing. The dark, tarry distillation residue was not examined. Two recrystallizations of the desired product from methanol-water gave white crystals: mp $45\text{--}46^\circ$; infrared (CS_2) bands for terminal methylene at 1660 (medium) and 886 (very strong), and for hindered hydroxyl at 3675 cm^{-1} (medium, sharp); nmr peaks at τ 8.54 (18 H, sharp singlet, *t*-butyls), 8.23 (3 H, broad singlet, methyl group attached to double bond), 7.15–7.95 (4 H, multiplet, contiguous methylene groups), 5.28 (2 H, broad singlet, olefinic protons), 5.03 (1 H, sharp singlet which shifted downfield upon acidification, hydroxyl proton), and 3.03 (2 H, sharp singlet, aromatic hydrogens). The mass spectrum (70 v) showed a very strong peak at m/e 219; its intensity was 10 times greater than that of the parent

(35) M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).

peak at m/e 274. The low yield in this preparation may have been caused largely by incomplete formation of the Grignard reagent.

Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.52; H, 11.11.

Preparation of 2-*t*-Butyl-6-chloro-*p*-cresol (20).—A mixture of 2-*t*-butyl-*p*-cresol (16.4 g, 100 mmoles) and sulfuryl chloride (13.5 g, 100 mmoles) was stirred at room temperature for 2.5 hr and then warmed at 60° until gas evolution ceased (45 min). Benzene (100 ml) was added, and the solution was washed with two 50-ml portions each of 20% aqueous sodium hydroxide and saturated aqueous sodium chloride. After drying and concentration by evaporation, the organic phase was distilled to give a fraction, bp 105–106° at 10 mm, which proved to be pure 20 (11.55 g, 58% yield). The infrared and nmr spectra of this material were the same as those of the product formed from peroxydienone 1a by the action of hydrogen chloride in benzene (see above).

Preparation of 2,6-Di-*t*-butyl-4-chlorophenol (25).—Phenol 14 (10.0 g, 48.5 mmoles) was heated under reflux with sulfuryl chloride (6.55 g, 48.5 mmoles) until gas evolution had nearly stopped (1.5 hr), and the mixture was then allowed to stand at room temperature overnight. After dissolution in ether (100 ml), the mixture was washed with two 30-ml portions of 3 *N* sodium carbonate solution, dried, concentrated by evaporation, and distilled. The material collected at 106° (1.9–2.1 mm) solidified on cooling and afforded 3.47 g (30% yield) of 25, mp 75.5–77° (lit.³⁶ mp 75–76°) after recrystallization from methanol-water. A further recrystallization from cold methanol gave snow white needles melting at 77–78.5°. The structure was confirmed by an nmr spectrum ($CDCl_3$), which exhibited sharp singlets at τ 8.56 (18 H, *t*-butyls), 4.96 (1 H, hydroxyl), and 2.96 (2 H, aromatic hydrogens).

Preparation of 2,6-Di-*t*-butyl-4-chloro-4-methyl-2,5-cyclohexadien-1-one (22).—A mixture of 10 (50.0 g, 0.227 mole), glacial acetic acid (100 ml), and methanol (100 ml) was cooled to –12° and stirred while slightly more than 1 equiv of chlorine gas was introduced. The temperature rose to –10° during the addition, which required 3 min, and a considerable amount of solid separated. The mixture was filtered immediately, and the recovered solid was washed twice with Dry Ice chilled methanol. After air drying in the refrigerator for several days, the product (28.0 g) melted at 90–95°. Two additional crops, mp 91–95° (6.0 g) and 88–91° (6.7 g), precipitated when the cold mother liquor was concentrated *in vacuo*; these were recovered in a similar manner. All three crops were combined and recrystallized from cold petroleum ether (bp 30–60°) to give 21.9 g (38% yield) of 22 as cream-colored needles, mp 100–101.5° (lit.³⁷ mp 103°). The nmr spectrum ($CDCl_3$) showed sharp singlets at τ 8.74 (18 H, *t*-butyl groups), 8.23 (3 H, 4-methyl group), and 3.42 (2 H, ring protons). When methanol was used as the recrystallization solvent, the desired product was not obtained; instead, the precipitated solid proved to be 2,6-di-*t*-butyl-4-methoxy-4-methyl-2,5-cyclohexadien-1-one, tiny, snow white needles melting at 92.5–93° (lit.^{12a} mp 94°). The nmr spectrum ($CDCl_3$) of the methoxydienone consisted of sharp singlets at τ 8.77 (18 H, *t*-butyls), 8.68 (3 H, 4-methyl group), 6.90 (3 H, methoxy group), and 3.58 (2 H, protons on ring).

Reactions of 22 with Hydrogen Chloride in Benzene.—A solution of chlorodienone 22 (1.27 g, 4.98 mmoles) in 65 ml of anhydrous benzene was saturated with gaseous hydrogen chloride and allowed to stand under the usual conditions for 121 hr.

Evaporation of volatile constituents left 1.03 g of oil whose infrared spectrum (neat sample) differed from that of pure chlorophenol 20 in only minor respects. Analysis by gas chromatography (column B) showed that the oil consisted of 20 (96 area %, 99% yield) and small amounts of materials with longer retention times. A similar experiment using a reaction time of 17 hr gave 20 in 94% yield.

In a further experiment, a solution of 22 (1.27 g, 4.98 mmoles) and 14 (10.25 g, 49.7 mmoles) in 55 ml of dry benzene was saturated with hydrogen chloride and allowed to react for 121 hr under the usual conditions. Gas chromatographic analysis (column B) of the residual oil showed that its only constituents were 14, 15 (11% yield), 17 (1% yield, based on 14), and 20 (89% yield) (sum of yields of 15 and 20 equated to 100% for normalization). All products were identified by the usual comparisons with pure reference compounds.

Chlorinations with Hydrogen Chloride and *t*-Butyl Hydroperoxide.—A solution of *t*-butyl hydroperoxide (91.7% pure, 0.49 g, 4.99 mmoles) and phenol 14 (2.05 g, 9.94 mmoles) in dry benzene (63 ml) was saturated with hydrogen chloride gas and allowed to react under the usual conditions for 118 hr. The mixture was then worked up in the usual way. Analysis of the carbonate-insoluble organic residue (2.06 g) by gas chromatography (column B) revealed four principal peaks (99.7% of the total area); these were trapped separately and shown to be unreacted 14 (63% recovery), chlorophenol 25 (59% yield, based on hydroperoxide), 17 (1% yield, based on 14), and 27 (2% yield, based on 14) by the usual comparisons.

An analogous experiment was performed starting with 14 (1.03 g, 5.00 mmoles), 10 (1.10 g, 5.00 mmoles), and *t*-butyl hydroperoxide (91.7% pure, 0.49 g, 4.99 mmoles) in dry benzene (64 ml). Work-up after 97 hr afforded 2.06 g of product which was shown by gas chromatography (column B) to consist of 10 (62% recovery), 14 (53% recovery), 20 (20% yield), and 25 (31% yield), together with small amounts of 17, 27, and unidentified materials. The structures of the identified compounds were confirmed in the usual way.

Preparation of 2,6-Di-*t*-butylhydroquinone Diacetate (34).—Sulfuric acid catalyzed acetylation of 2,6-di-*t*-butylhydroquinone in boiling acetic anhydride has been reported to give 34 in 59.8% yield.³⁸ In the present work better results were obtained with the following procedure.

A solution of 2,6-di-*t*-butylhydroquinone³⁹ (1.50 g, 6.75 mmoles) and concentrated sulfuric acid (0.10 ml) in 20 ml of acetic anhydride was allowed to react under our usual conditions for 24 hr. Work-up in the usual way gave 1.98 g (96% yield) of 34 in essentially pure form, mp 103–106° (lit.³⁸ mp 101.5–102.5°) alone, mp 57–75° upon admixture with a sample of the starting hydroquinone having mp 104–105.5° (lit.³⁹ mp 110–111°). Recrystallization of the diacetate from methanol-water gave material melting at 105.5–106.5°. The nmr spectrum ($CDCl_3$) showed singlets at τ 8.64 (18 H, *t*-butyl groups), 7.76 (3 H, probably arising from the 4-acetoxy group), 7.69 (3 H, 1-acetoxy substituent ?), and 2.96 (2 H, aromatic hydrogens). Bands appeared in the carbonyl region of the infrared spectrum (CS_2) at 1775 (strong) and 1735 cm^{-1} (medium); no hydroxyl absorption was detected.

Acknowledgments.—The author is indebted to Mr. H. J. Tarski for excellent technical assistance and to Dr. F. H. Field for his continued interest and encouragement.

(36) H. Hart and F. A. Cassis, Jr., *J. Am. Chem. Soc.*, **73**, 3179 (1951).

(37) M. Pestemer, German Patent 936,684 (1955).

(38) J. Pospíšil and L. Taimr, *Collection Czech. Chem. Commun.*, **29**, 381 (1964).

(39) E. Müller and K. Ley, *Ber.*, **88**, 601 (1955).