tions indicated the presence of small amounts of other styrenes, one of them due to a reversed addition of the disiamylborane to phenylacetylene. Bands due to the *cis* isomer were not evident.

Trimethyl-*sec*-butyltin. *sec*-Butylmagnesium bromide was prepared from 54.9 g (0.4 mole) of *sec*-butyl bromide and 14.6 g (0.6 g-atom) of magnesium in 400 ml of dry ether. The Grignard reagent was separated from excess magnesium by forcing it with argon pressure through a glass tubing with a glass wool filter into another flask. Trimethyltin chloride (39.9 g, 0.2 mole) in 50 ml of ether was added at 20° and the mixture heated to reflux for 2 hr and hydrolyzed after cooling by pouring onto ice and ammonium chloride. The organic layer was separated, dried over calcium chloride, and fractionated over a 20-cm column packed with glass helices to yield 28.5 g (64%) of product, bp 145.5–146° (760 mm), n^{20}D 1.4614. Glpc analysis indicated a purity of 99% (6-ft silicone rubber SE 30 10% on Diatoport W 60–80, 70° isothermal). *Anal.* Calcd for $C_7H_{18}Sn$: Sn, 53.73. Found: Sn, 53.38.

Addition of Organotin Hydrides to Olefins. Ampoules of Pyrex glass were evacuated, heated, and filled with argon. Organotin hydride (1.5 mmoles) and styrene or hexene (6 mmoles) were placed in the ampoule under a steady stream of argon and sealed after cooling to −78°. The ampoules were then heated or irradiated with a 100-w, medium-pressure mercury vapor lamp. The excess olefin was recovered by distillation (10 mm) into a trap cooled to −78°, and analyzed by infrared spectroscopy. In the reactions with *cis*- and *trans*-2-butenes 0.3–0.4 g (about 6 mmoles) of the olefin was condensed from the tank into the air-free ampoule at −78°, and 1.0 ml of an organotin hydride was added. The ampoules were sealed and irradiated with a 100- or 250-w lamp as described above. The recovered 2-butenes were analyzed by glpc (15-ft dimethylsulfolane 28% on crushed Firebrick, 0°, isothermal). After the trapping of butenes, the remaining liquids were analyzed by glpc. When tri-*n*-butyltin hydride was used, small amounts of tetrabutyltin and hexa-*n*-butylditin were found (4-ft silicone rubber SE 30 20% on Chromosorb W 60–80, 240° isothermal). When trimethyltin hydride was used, trimethyl-*sec*-butyltin was formed along with small amounts of tetramethyltin and hexamethylditin. It was separated by distillation [bp 146–148° (760 mm)]. Its infrared and nmr spectra were found to be identical with those of an authentic sample.

Inhibition of Free-Radical Reactions. IV.
The Synergistic Effect of 2,6-Di-*t*-butylphenols on Hydrocarbon Oxidation Retarded by 4-Methoxyphenol

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Abstract: By means of stop-flow studies it has been demonstrated that the rate of reaction of the 4-methoxyphenoxy radical with 2,4,6-tri-*t*-butylphenol is 425–850 times faster than interaction with 9,10-dihydroanthracenyl hydroperoxide and 7400–14,800 times faster than its reaction with 9,10-dihydroanthracene at 60° in chlorobenzene. The effects of the addition of 2,6-di-*t*-butylphenols on the rates of oxygen absorption of 9,10-dihydroanthracene retarded by 4-methoxyphenol have been determined over wide ranges of concentration. At low ratios of the concentrations of 4-methoxyphenol to hydrocarbon, the results for 2,6-di-*t*-butyl-4-methylphenol are quantitatively described by a kinetic scheme which involves the regeneration of 4-methoxyphenol by means of its radical reacting with the hindered phenol and the termination of the hindered phenoxy radical by reaction with peroxy radicals. In the case of 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butylphenol the termination involves both peroxy and phenoxy radicals with the hindered phenoxy radical. As the ratio of the concentrations of 4-methoxyphenol to hydrocarbon is increased, the oxidation results obtained upon the addition of the three hindered phenols are described by a scheme which involves a fast equilibrium between the 4-methoxyphenoxy radical and the hindered phenoxy radical and termination by both dimerization of the 4-methoxyphenoxy radical and the reaction of the 4-methoxyphenoxy radical with the hindered phenoxy radical. The analysis of these kinetic results reveal that (1) the value of the rate constant for the reaction of 2,6-di-*t*-butyl-4-methylphenoxy with the peroxy radical is considerably larger than $8.7 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, (2) the rate constant for the dimerization of the 4-methoxyphenoxy radical is smaller than $1 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, (3) the rate constant for hydrogen abstraction by the 4-methoxyphenoxy radical from 9,10-dihydroanthracene is smaller than $115\ M^{-1}\ \mathrm{sec}^{-1}$, and (4) the equilibrium constant for hydrogen transfer between peroxy radicals and 4-methoxyphenol is larger than 50. In agreement with the kinetic results, the addition of the hindered phenols have a dramatic synergistic effect on the length of the inhibition period produced by 4-methoxyphenol. The quinol ether produced by reaction of 4-methoxyphenoxy and 2,4,6-tri-*t*-butylphenoxy has been shown to function as an inhibitor at low concentrations and as an initiator at concentrations greater than $2 \times 10^{-3}\ M$. This observation and results of ancillary experiments suggest that this compound is in equilibrium with its precursors. In addition it has been demonstrated that 3,5,3′,5′-tetra-*t*-butylstilbene-4,4′-quinone is produced only upon evaporation of a solution of 2,6-di-*t*-butylquinone-4-methide, produced by the reaction of peroxy radicals with mixtures of 4-methoxyphenol and 2,6-di-*t*-butyl-4-methylphenol. The results of the kinetic, *inhibition period*, and product studies for this system have been related to the general phenomenon of antioxidant synergism manifested by mixtures of hindered and nonhindered phenols. A correlation has been demonstrated between the magnitude of synergism observed in practice and the competition between hydroperoxide and hindered phenoxy for the nonhindered phenoxy radical as measured in the laboratory.

The rates of oxygen absorption of solutions of 9,10-dihydroanthracene (DHA) and 2,2′,3,3′-tetraphenylbutane (TPB) containing hindered phenols or hydroquinones have been explained by a relatively simple rate equation.[1] The expression was derived from a scheme

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[1] L. R. Mahoney, *J. Am. Chem. Soc.*, **88**, 3035 (1966).

that involves a simple competition between the hydrocarbon and the phenolic compound for the chain carrying peroxy radical. These results are consistent with the view that these phenoxy and semiquinone free radicals, formed in the reaction with peroxy radicals, are either destroyed by rapid termination reactions or, equivalently, are too hindered or too unreactive to engage in chain restarting reactions. In contrast, the experimental rates of oxidation of solutions of DHA and TPB containing nonhindered phenols required a complex rate equation[2] for their explanation. This expression was derived from a scheme in which the chain restarting reactions of the phenoxy radical with hydroperoxide and/or hydrocarbon were included. The numerical results obtained by means of this analysis are consistent with the view that (1) the relative rates of destruction of phenoxy radicals by dimerization and by reaction with peroxy radical are extremely sensitive to the structure of the phenoxy radical and that (2) compounds such as 4-methoxyphenol yield phenoxy radicals which are very highly selective in hydrogen transfer reactions as compared to peroxy radicals.

Experimental techniques, recently developed in this laboratory, have allowed the detailed examination of the absolute rates of reaction of a free radical derived from the first class of phenols, 2,4,6-tri-*t*-butylphenoxy, with a number of nonhindered phenols and of the products formed in these reactions.[3] The results of that investigation revealed that 2,4,6-tri-*t*-butylphenoxy is also very highly selective in its hydrogen atom transfer reactions and that its rates of reaction with nonhindered phenoxy radicals compete very favorably with the rates of dimerization of these species.

These large differences in the chemical reactivity between peroxy, 4-methoxyphenoxy, and 2,4,6-tri-*t*-butylphenoxy radicals in their hydrogen abstraction reactions and their apparent specificity in modes of termination suggest that a system in which all three species are simultaneously generated should manifest unique behavior. A study of this nature should provide a severe test of the interpretation of the earlier work and would hopefully yield further information regarding the chemistry of phenoxy radicals. The present work describes the results of such a study.

Results and Discussion

I. Kinetic Studies. In the preceding paper of this series[2] the rates of oxidation of the 9,10-dihydroanthracene (DHA)-2,2′,3,3′-tetraphenylbutane system containing 4-methoxyphenol were shown to be accurately described by a general rate expression derived from the following kinetic scheme.

$$\text{R-R} \xrightarrow{k_1} 2\text{R}\cdot \qquad (1)$$

$$\text{R}\cdot + \text{O}_2 \xrightarrow{k_2} \text{RO}_2\cdot \qquad (2)$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{k_3} \text{RO}_2\text{H} + \text{R}\cdot \qquad (3)$$

$$2\text{RO}_2\cdot \xrightarrow{k_4} \text{O}_2 + \text{inert products} \qquad (4)$$

$$\text{RO}_2\cdot + \text{AH} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \text{RO}_2\text{H} + \text{A}\cdot \qquad (5, -5)$$

$$\text{A}\cdot + \text{RO}_2\cdot \xrightarrow{k_6} \text{inert products} \qquad (6)$$

$$2\text{A}\cdot \xrightarrow{k_7} \text{inert products} \qquad (7)$$

$$\text{A}\cdot + \text{RH} \xrightarrow{k_8} \text{AH} + \text{R}\cdot \qquad (8)$$

where R–R is the source of free radicals, R· and RO$_2$· are the hydrocarbon and peroxy radicals, and AH and A· represent 4-methoxyphenol and the 4-methoxyphenoxy radical. Upon the addition of a hindered phenol, BH, to a system containing 4-methoxyphenol the additional reactions

$$\text{A}\cdot + \text{BH} \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \text{AH} + \text{B}\cdot \qquad (9, -9)$$

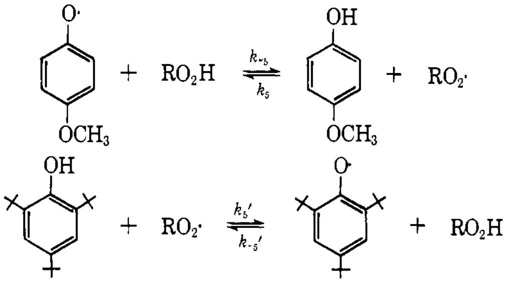
$$\text{RO}_2\cdot + \text{BH} \xrightarrow{k_5'} \text{RO}_2\text{H} + \text{B}\cdot \qquad (5')$$

$$\text{A}\cdot + \text{B}\cdot \xrightarrow{k_{10}} \qquad (10)$$

$$\text{RO}_2\cdot + \text{B}\cdot \xrightarrow{k_{11}} \qquad (11)$$

must be included in the scheme. The possible chain restarting reactions of B·, *i.e.*, $-5'$ and -9, may be excluded from the analysis. Previous oxidation studies[2] have shown that their rates of reaction are too slow to be kinetically important.

A. Estimate of the Values of k_9/k_5 and k_9/k_8. The value of the equilibrium constant, k_9/k_{-9}, for the 4-methoxyphenoxy-2,4,6-tri-*t*-butylphenol system is equal to the product of the equilibrium constants for the reactions



i.e., $k_9/k_{-9} = (k_{-5}/k_5)(k_{5'}/k_{-5'})$. Rearranging we may write

$$k_9/k_{-5} = (k_{5'}/k_5)(k_{-9}/k_{-5'}) = (k_{5'}/k_3)(k_{-9}/k_{-5'})/(k_5/k_3)$$

The values of $k_{5'}/k_3$, 17.5,[1] and k_5/k_3, 284,[2] have been determined by oxygen absorption studies at 60° in chlorobenzene. We now turn our attention to the determination of the values of k_{-9} and $k_{-5'}$ under the same conditions.

By means of stop-flow spectrophotometric techniques the absolute values of the rate constants for hydrogen abstraction from a number of substituted phenols by the 2,4,6-tri-*t*-butylphenoxy radical at 24° in benzene have been determined in this laboratory.[3] The rates of hydrogen abstraction from tetralyl hydroperoxide and from 9,10-dihydroanthracenyl hydroperoxide, reaction $-5'$, have now been examined at 24 and 60° by means of the same techniques. As in the case of the phenols reported earlier the reaction is irreversible, *i,e.*, $k_{11}\cdot(\text{B}\cdot) >> k_5(\text{BH})$, under the conditions of the experiment. As shown in Table I a change of solvent from pure benzene to 90% chlorobenzene has little effect on the value of rate constants or on the value of their temperature coefficients. The difference in the values

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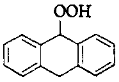
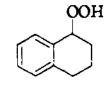
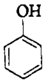
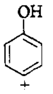
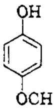
[2] L. R. Mahoney, *J. Am. Chem. Soc.*, **89**, 1895 (1967).

[3] M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, **32**, 1 (1967).

Table I. Summary of Second-Order Rate Constants for Hydrogen Abstraction by the 2,4,6-Tri-*t*-butylphenoxy Radical

Compound	Solvent	Temp,[a] °C	Rate constant,[b] M^{-1} sec	Ref
	Benzene	24	0.20 ± 0.02	*c*
	90% chlorobenzene	24	0.176 ± 0.01	*c*
	90% chlorobenzene	60	0.87 ± 0.04	*c*
	90% chlorobenzene	24	0.69 ± 0.06	*c*
	90% chlorobenzene	60	2.01 ± 0.15	*c*
	Benzene	24	6.17 ± 0.47	*d*
	Benzene	60	16.9 ± 1.5	*c*
	90% chlorobenzene	60	16.2 ± 1.6	*c*
	Benzene	24	92.5 ± 6.5	*d*
	Benzene	60	245 ± 12.3	*c*
	90% chlorobenzene	60	219.0 ± 11.0	*c*
	Benzene	24	6060 ± 235	*d*

[a] Uncertainties in temperature ±0.5° at 24.0° and ±0.02° at 60°. [b] All volumes corrected for temperature. [c] This work. [d] M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, **32**, 1 (1967).

of the rate constants for the two hydroperoxides is no doubt due to steric effects.[4]

The value of k_{-9}, equal to 6060, for 4-methoxyphenol was determined by esr at 24° in benzene.[3] Due to the limitation of the present esr equipment in regard to temperature control, we did not attempt to measure the value of this constant at 60° in chlorobenzene. However, an estimate, sufficiently accurate for our purposes here, of the effect of temperature and solvent on the value of this constant can be made. In Table I are summarized the values of k_{-9} for phenol and 4-*t*-butylphenol. The change in solvent from pure benzene to 90% chlorobenzene has little effect on the rate constants or on their temperature coefficients.

If the activation energy, $\Delta E^{\ddagger}{}_{-9}$, for 4-methoxyphenol is smaller than or equal to the value obtained for 4-*t*-butylphenol, 4.5 kcal/mole, the value of k_{-9} for 4-methoxyphenol at 60° will be between 6000 and 12,000 M^{-1} sec^{-1}. We may now substitute this value and the value of $k_{-5'}$, the rate constant obtained for the hydrogen abstraction from 9,10-anthracenyl hydroperoxide by 2,4,6-tri-*t*-butylphenoxy, to obtain k_9/k_{-5}, *i.e.*

$$k_9/k_{-5} = (k_{5'}/k_3)(k_{-9}/k_{5'})/(k_5/k_3) = (17.5/284)[(6000\text{–}12{,}000)/0.87] = 425\text{–}850$$

Since the value of k_{-5}/k_8, 17.5, has been previously determined for the 4-methoxyphenoxy radical,[2] we may obtain the ratio of k_9/k_8 by the following relationship

$$k_9/k_8 = (k_9/k_{-5})(k_{-5}/k_8) = (425\text{–}850)(17.5) = 7400\text{–}14{,}800$$

The value of k_9/k_8 for 2,6-di-*t*-butyl-4-methylphenol[5] should be larger than or equal[6] to that of the tri-*t*-butyl compound while the value of the same ratio for 2,6-di-*t*-butylphenol should be significantly smaller.

B. Oxygen Absorption Studies. The general rate expression which accurately describes the rates of oxygen absorption of the DHA–TPB system at 60° in the presence of a nonhindered phenol, AH, is

$$\frac{1}{[2k_1(\text{RR})]^{1/2}(\text{RH})}\left[\frac{d(\text{O}_2)}{dt} - 2k_1(\text{RR})\right] = \frac{1+\alpha}{\left[\dfrac{2k_4}{k_3{}^2} + \dfrac{2k_6}{k_3k_8}\alpha + \dfrac{2k_7}{(k_8)^2}\alpha^2\right]^{1/2}} \tag{I}$$

where $\alpha = (\text{AH})/[(k_3/k_5)(\text{RH}) + (k_{-5}k_3/k_8k_5)(\text{RO}_2\text{H})]$. The values of the parameters for AH equal to 4-methoxyphenol[2] are: $(k_3/k_5) = 3.53 \times 10^{-3}$, $(k_{-5}/k_8) = 17.5$, $(2k_6/k_8k_8) = 4.96 \times 10^4$ M sec, and $(2k_7/k_8{}^2) = 2.54 \times 10^3$ M sec.

When the ratio of (RH)/(RO_2H) is much larger than k_{-5}/k_8, as is the case for all data reported here, the fraction of the oxidation rate due to hydrogen abstraction by the 4-methoxyphenoxy radical from hydrocarbon, reaction 8, is equal to $\gamma/(1 + \gamma)$ where γ is defined as the quantity $(k_5/k_3)[(\text{AH})/(\text{RH})]$. For convenience of discussion the kinetic results obtained with added hindered phenol are divided into two sections: where γ is much smaller than 1 and where the value of γ is much larger than 1.

1. Concentration Range with γ Smaller Than 1. At these high ratios of 9,10-dihydroanthracene to 4-methoxyphenol there are two possible chain carrying species, the peroxy radical and the 4-methoxyphenoxy radical, and in the presence of the hindered phenols a general kinetic analysis is not possible. However, the results of this portion of the study may be analyzed by the following considerations. Under conditions in which RH/BH << k_9/k_8 and if $k_{10}(\text{A}\cdot) + k_{11}(\text{RO}_2\cdot) \gg k^{-}{}_9(\text{AH})$, reaction 8 would be completely suppressed and all of the oxidation occurs *via* reaction 3, *i.e.*

$$d(\text{O}_2)/dt = 2k_1(\text{RR}) + k_3(\text{RO}_2\cdot)(\text{RH})\cdot$$

At steady state

$$2k_1(\text{RR}) = qk_5(\text{RO}_2\cdot)(\text{AH}) + qk_{5'}(\text{RO}_2\cdot)(\text{BH})$$

and the rate expression obtained would be of the form

$$\frac{d(\text{O}_2)}{dt} = 2k_1(\text{RR}) + 2k_1(\text{RR})\frac{k_3(\text{RH})}{qk_5(\text{AH}) + qk_{5'}(\text{BH})} \tag{II}$$

The value of q would equal unity if termination is exclusively by means of reaction 10. If reaction 11 is the sole mode of termination, then the value of q would equal 2.

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[4] These steric effects for 2,6-di-*t*-butylphenols manifest themselves in reaction 5, the reverse reaction. For example, the relative values of k_5 for the series 2,4,6-tri-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol, 1-hydroxynaphthalene, and 1,4-dihydroxybenzene are in the ratio 1.00:1.39: 3.88:2.76 for the tetralylperoxy radical at 50°; *cf.* D. S. Davies, H. L. Gupta, and G. R. Lester, *J. Chem. Soc.*, 4926 (1956). The same ratios are 1.00:1.11:8.35:8.91 for the bulkier 9,10-dihydroanthracenyl peroxy radical at 60°.[1]

[5] An attempt was made to generate the 2,6-di-*t*-butyl-4-methylphenoxy radical by mixing concentrated solutions of the phenol (45–184 × 10^{-4} M) with solutions of the 2,4,6-tri-*t*-butylphenoxy radical (8 × 10^{-4} M) under flow conditions. If the hydrogen atom transfer between the two species was rapid compared to the disproportionation of the 4-methyl-substituted radical a convenient technique for examining the reactivity of the 2,6-di-*t*-butyl-4-methylphenoxy radical in reaction −9 could be developed. However, the rate of decay of radicals at these concentrations was dependent on the concentration of 2,6-di-*t*-butyl-4-methylphenol. Thus the value of k disproportionation >> $50k$ hydrogen atom transfer.

[6] This argument is based upon the relative reactivities of the hindered phenols toward the anthracenylperoxy radical.

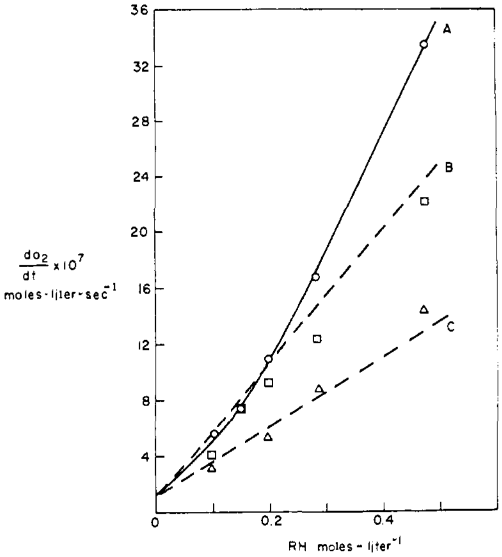

Figure 1. Rate of oxygen absorption *vs.* hydrocarbon concentration. The concentration of TPB is 0.3×10^{-3} *M* and the concentration of 4-methoxyphenol is $8.6 \pm 0.2 \times 10^{-5}$ *M* in all cases: ○, no added hindered phenol; □, $4.3 \pm 0.1 \times 10^{-5}$ *M* 2,4,6-tri-*t*-butylphenol added; △, $4.3 \pm 0.1 \times 10^{-5}$ *M* 2,6-di-*t*-butyl-4-methylphenol added.

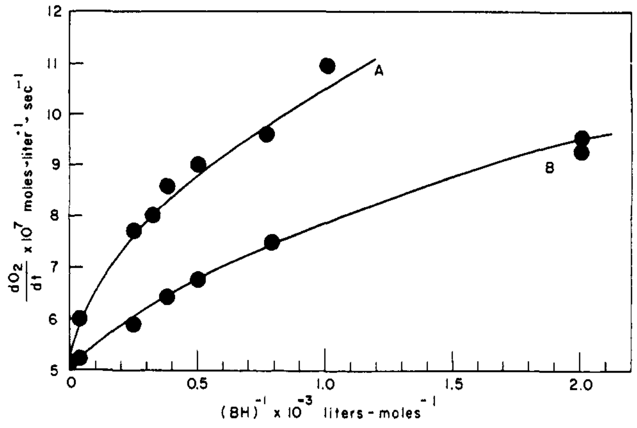

Figure 2. Rate of oxygen absorption *vs.* the [concentration]$^{-1}$ of 2,6-di-*t*-butyl-4-methylphenol: curve A, RH equal to 0.196 *M* and 4-methoxyphenol equal to 30×10^{-3} *M*; curve B, RH equal to 0.099 *M* and 4-methoxyphenol equal to 30×10^{-3} *M*.

Since the values of k_5/k_3 and $k_{5'}/k_3$ have been obtained from oxidation studies with the individual compounds, it is possible to calculate the rates of oxygen absorption of the mixture under these conditions. In Figure 1 are presented the data for the rates of oxygen absorption in the presence and in the absence of added hindered phenol as a function of hydrocarbon concentration. Curve A is calculated from eq I utilizing the parameters for 4-methoxyphenol previously reported.[2] The solid curves B and C were calculated from eq II with q equal to 1 and to 2.

The mixture of 4-methoxyphenol and 2,6-di-*t*-butyl-4-methylphenol yields rates of oxidation which agree quite well with those calculated from eq II with q equal to 2. As shown in Table II, when the concentration of 4-methoxyphenol, AH, is less than or equal to 1×10^{-4} *M*, the rate of oxygen absorption is first order in hydrocarbon and first order in TPB. Although the order in AH and BH is complex, at a constant ratio of AH/BH the rate is inversely proportional to the concentration of BH in agreement with eq II. As the concentration of 4-methoxyphenol is increased above 2×10^{-4} *M*, the observed rate of oxygen absorption is higher than that calculated from eq II with q equal to 2. The source of this divergence may be either that the rate of reaction -9 approaches the rate of termination reaction 11 or that the termination reaction 10 becomes more important due to the increase in the steady-state concentration of A· and the corresponding decrease in the steady-state concentration of $RO_2\cdot$.

In contrast to the 4-methyl compound, 2,4,6-tri-*t*-butylphenol fails to obey eq II over a wide range of concentrations. The oxidation data for this compound are summarized in Table II. The kinetic order in hydrocarbon is approximately one while the dependence on TPB concentration is complex. At low TPB concentrations and AH concentrations greater than 1×10^{-4} *M*, the rate is independent of both AH and BH concentrations. This result is consistent with the view that the requirement $k_{11}(RO_2\cdot) + k_{10}(A\cdot) >> k_{-9}(AH)$ is not fulfilled for the 2,4,6-tri-*t*-butylphenoxy radical under these conditions. At lower concentrations of AH the apparent value of q lies between 1 and 2 suggesting the simultaneous occurrence of the termination reactions 10 and 11. The complex chemistry of the product of reaction 10, which qualitatively accounts for the kinetic results observed with this hindered phenol, is described in a latter section of this work.

The oxidation data for 2,6-di-*t*-butylphenol are consistent with the view that a mixed termination is also occurring with the hindered phenoxy radical. At higher levels of 4-methoxyphenol and low concentrations of TPB the rate again becomes independent of the concentration of 4-methoxyphenol. The product of reaction 10 would be a 2,6-di-*t*-butyl-4-phenoxyphenol, a strong inhibitor capable of stopping two chains.[7]

2. Concentrations with γ Much Larger Than 1. At high concentrations of 4-methoxyphenol the rates of oxygen absorption of solutions containing 9,10-dihydroanthracene and TPB are independent of the concentration of 4-methoxyphenol,[2] and are accurately described by the expression

$$\frac{d(O_2)}{dt} = 2k_1(RR) + \frac{k_8}{(2k_7)^{1/2}}[2k_1(RR)]^{1/2}(RH)$$

This expression represents a limiting case of eq I and is consistent with a kinetic scheme in which the rate-controlling reactions are 1, 7, and 8. Due to the high concentrations of 4-methoxyphenol all peroxy radicals produced from TPB and from the substrata are rapidly converted to the 4-methoxyphenoxy radical.

The value of k_5/k_3 for 4-methoxyphenol is 284, while the values of $2k_5/k_3$ for 2,6-di-*t*-butylphenol, 2,4,6-tri-*t*-butylphenol, and 2,6-di-*t*-butyl-4-methylphenol are 10.8, 35.0, and 38.5, respectively.[1] As a result of these differences in reactivity even at ratios of 4-methoxyphenol to hindered phenol equal to unity, only a few per cent of the peroxy radicals react with the hindered phenol. The addition of much smaller amounts of the hindered phenol results in the retardation of the oxygen rate. Typical experimental results for 2,6-di-*t*-butyl-4-methylphenol are shown in Figure 2 and the data for 2,6-di-*t*-butylphenol and 2,4,6-tri-*t*-butylphenol are

(7) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 43, 2724 (1965).

Table II. Summary of Oxygen Absorption of the 9,10-Dihydroanthracene–TPB–4-Methoxyphenol System (γ smaller than 1) with Added Hindered Phenol

AH × 10^3 *M*	BH × 10^3 *M*	TPB × 10^3 *M*	RH × 10^3 *M*	Rate × 10^7 *M* sec^{-1}	Kinetic chain length[a] Obsd	Kinetic chain length[a] Calcd	RH/BH
			2,6-Di-*t*-butyl-4-methylphenol[b]				
0.0445	0.089	0.31	99	5.61	3.52	3.42	1,110
0.050	0.0100	0.31	148	6.80	4.50	4.57	1,480
0.0435	0.087	0.31	242	12.55	9.14	8.59	2,780
0.025	0.050	0.31	148	12.50	10.2	9.15	2,960
0.042	0.084	0.31	469	26.40	20.6	17.25	5,580
0.020	0.040	0.31	469	52.0	42.0	36.2	11,725
0.089	0.089	0.31	99	3.66	1.81	1.83	1,110
0.100	0.100	0.31	148	3.70	2.00	2.44	1,480
0.050	0.050	0.31	148	7.20	4.80	4.87	2,960
0.0895	0.0872	0.12	469	6.03	10.48	8.86	5,380
0.084	0.084	0.31	469	13.44	9.74	8.86	5.380
0.084	0.084	0.31	469	13.38	9.75	8.86	5,380
0.084	0.084	0.61	469	26.40	9.68	8.86	5,380
0.084	0.084	1.23	469	53.60	9.90	8.86	5,380
0.0447	0.0436	0.12	469	11.10	21.0	17.75	10,760
0.0179	0.0174	0.12	469	29.0	59.10	44.50	27,000
0.200	0.100	0.31	99	2.40	2.40	0.84	990
0.200	0.100	0.31	148	3.20	1.58	1.26	1,480
0.089	0.045	0.31	99	2.92	1.44	1.87	2,200
0.200	0.100	0.31	242	4.10	2.31	2.12	2,420
0.100	0.050	0.31	148	4.20	2.34	2.50	2,960
0.087	0.043	0.31	196	5.45	3.40	3.88	4,560
0.087	0.043	0.31	281	8.89	6.17	5.57	6,540
0.084	0.042	0.31	469	14.80	9.06	9.95	11,800
0.300	0.05	0.31	148	3.20	1.58	1.69	2,960
1.00	0.05	0.31	148	3.80	2.06	0.516	2,960
			2,4,6-Tri-*t*-butylphenol[c]				
0.025	0.050	0.31	148	13.2	9.65	18.54	2,960
0.100	0.100	0.62	196	12.60	4.0	6.51	1,960
0.100	0.100	0.31	196	7.60	5.16	6.51	1,960
0.100	0.100	0.15	196	4.60	5.66	6.51	1,960
0.100	0.100	0.075	196	2.40	7.00	6.51	1,960
0.05	0.05	0.31	469	44.90	35.0	31.2	9,380
0.025	0.025	0.31	469	78.20	62.0	62.4	18,750
0.089	0.045	0.31	99	3.92	2.16	3.88	2,200
0.0886	0.0443	0.31	148	7.44	5.00	5.89	3,340
0.088	0.044	0.31	196	9.20	6.42	7.87	4,460
0.087	0.043	0.31	281	12.46	9.05	11.50	6,530
0.084	0.042	0.31	469	22.06	16.8	19.68	11,150
0.100	0.05	0.075	196	2.40	7.00	6.92	3,920
0.200	0.100	0.075	196	2.40	7.00	6.92	3,920
0.400	0.100	0.075	196	2.50	7.30	3.41	3,920
			2,6-Di-*t*-butylphenol[d]				
0.10	0.10	1.22	148	19.4	2.97	5.02	1,480
0.05	0.05	0.31	148	10.6	7.57	10.0	2,960
0.20	0.10	1.22	148	15.4	2.35	2.56	1,480
0.089	0.045	0.31	99	4.94	3.07	3.80	2,200
0.100	0.050	0.31	148	6.3	4.08	5.12	2,960
0.0886	0.044	0.31	148	6.6	4.37	6.35	3,360
0.088	0.043	0.31	196	9.3	6.50	7.88	4,560
0.087	0.043	0.31	281	14.36	10.57	11.30	6,520
0.084	0.042	0.31	469	30.0	23.20	19.35	11,200
0.30	0.10	1.22	148	13.3	1.72	1.72	1,480
0.20	0.05	0.31	148	4.6	2.74	2.51	2,960
0.30	0.05	0.31	148	4.6	2.74	1.72	2,960

[a] Kinetic chain length is defined as $\{[d(O_2)/dt] - 2k_1(RR)\}/2k_1(RR)$. [b] The value of q for the calculated kinetic chain length was equal to 2. [c] The value of q for the calculated kinetic chain length was equal to 1. [d] The value of q for the calculated kinetic chain length was equal to 1.

summarized in Tables III and IV. A rate equation which gives a good description of the data is of the form

$$\frac{d(O_2)}{dt} = 2k_1(RR) + \frac{k_8}{(2k_7)^{1/2}}\,\frac{2k_1(RR)^{1/2}(RH)}{\left[1 + \frac{b(BH)}{(AH)}\right]^{1/2}} \qquad \text{(III)}$$

In the final columns of Tables III and IV are given the rates calculated with b equal to 655 and 460 for 2,6-di-*t*-butylphenol and 2,4,6-tri-*t*-butylphenol. The solid curves in Figure 2 were calculated with b equal to 800 for 2,6-di-*t*-butyl-4-methylphenol.

A kinetic scheme consistent with eq III involves (1), (7), (8), (9), (−9), and (10) as the kinetically important reactions. Under steady-state conditions

$$2k_1(RR) = 2k_7(A\cdot)^2 + 2k_{10}(A\cdot)(B\cdot)$$

and if

$$k_{-9}(AH) \gg k_{10}(A\cdot)$$

Table III. Summary of Calculated and Experimental Rates of Oxidation of 9,10-Dihydroanthracene Containing 4-Methoxyphenol and 2,6-Di-*t*-butylphenol (γ larger than 1)

4-Methoxyphenol $\times 10^3$ M	2,6-Di-*t*-butylphenol $\times 10^3$ M	RH $\times 10^3$ M	TPB $\times 10^3$ M	[d(O)/d*t*] $\times 10^7$ M sec^{-1} [a] Exptl	Calcd
60.0	0	99.0	1.23	17.3	18.72
60.0	1.0	99.0	1.23	9.0	8.80
60.0	2.0	99.0	1.23	8.6	7.75
60.0	4.0	99.0	1.23	7.4	6.93
60.0	8.0	99.0	1.23	6.1	6.36
60.0	1.0	196.0	1.21	11.5	12.36
60.0	2.0	196.0	0.61	6.8	6.42
60.0	2.0	196.0	1.21	10.2	10.04
60.0	2.0	196.0	2.47	16.8	17.68
30.0	0.5	99.0	1.23	8.8	8.69
30.0	1.0	99.0	1.23	8.0	7.85
30.0	2.0	99.0	1.23	7.4	6.93
30.0	1.0	196.0	1.21	10.5	10.34
30.0	2.0	196.0	1.21	9.1	8.80
30.0	3.0	196.0	1.21	8.2	8.10
30.0	4.0	196.0	1.21	8.2	7.68
30.0	8.0	196.0	1.21	7.0	6.84

[a] Values of $Kk_{10}/k_7 = 655$ and $k_8/(2k_7)^{1/2} = 19.8 \times 10^{-3}$ used for calculated rate.

Table IV. Summary of Calculated and Experimental Rates of Oxidation of 9,10-Dihydroanthracene Containing 4-Methoxyphenol and 2,4,6-Tri-*t*-butylphenol (γ larger than 1)

4-Methoxyphenol $\times 10^3$ M	2,6-Di-*t*-butylphenol $\times 10^3$ M	RH $\times 10^3$ M	TPB $\times 10^3$ M	[d(O)/d*t*] $\times 10^7$ M sec^{-1} [a] Exptl	Calcd
30.0	1.0	196.0	1.21	11.1	11.61
30.0	2.0	196.0	1.21	10.0	9.68
30.0	4.0	196.0	1.21	8.2	8.28
30.0	8.0	196.0	1.21	7.5	7.28
30.0	1.0	99.0	1.23	8.0	8.38
30.0	1.0	99.0	1.23	8.7	8.38
30.0	2.0	99.0	1.23	7.4	7.40
30.0	4.0	99.0	1.23	6.8	6.67
30.0	8.0	99.0	1.23	6.4	6.17
60.0	1.0	99.0	1.23	9.3	9.65
60.0	2.0	99.0	1.23	7.85	8.38
60.0	4.0	99.0	1.23	7.5	7.40
60.0	10.0	99.0	1.23	6.15	6.49
60.0	20.0	99.0	1.23	5.75	6.035
60.0	1.0	196.0	1.21	12.2	13.1
60.0	2.0	196.0	1.21	10.4	11.58
60.0	4.0	196.0	1.21	9.0	9.67
60.0	10.0	196.0	1.21	7.2	7.91
60.0	20.0	196.0	1.21	6.8	7.01

[a] Value of $Kk_{10}/k_7 = 460$ used for the calculated value and $k_8(2k_3)^{1/2} = 19.8 \times 10^{-3}$.

then

$$(\mathrm{B}\cdot) = (k_9/k_{-9})/[(\mathrm{BH})(\mathrm{A}\cdot)/(\mathrm{AH})]$$

Solving for the steady-state concentration of A·

$$(\mathrm{A}\cdot) = \left[\frac{2k_1(\mathrm{RR})}{2k_7 + 2k_{10}\dfrac{k_9}{k_{-9}}\dfrac{(\mathrm{BH})}{(\mathrm{AH})}}\right]^{1/2}$$

and the rate equation

$$\frac{-\mathrm{d}(\mathrm{O}_2)}{\mathrm{d}t} = 2k_1(\mathrm{RR}) + k_8(\mathrm{A}\cdot)(\mathrm{RH})$$

$$= 2k_1(\mathrm{RR}) + \frac{k_8}{(2k_7)^{1/2}}\left[\frac{2k_1(\mathrm{RR})}{1 + \dfrac{k_{10}}{k_7}\dfrac{k_9}{k_{-9}}\dfrac{(\mathrm{BH})}{(\mathrm{AH})}}\right]^{1/2}(\mathrm{RH})$$

The constant *b* represents the value of $(k_{10}/k_7)\ (k_9/k_{-9})$ for each hindered phenol.

C. Interpretation of Kinetic Parameters. In section B1 it was shown that the rates of oxygen absorption by mixtures of 4-methoxyphenol, AH, and 2,6-di-*t*-butyl-4-methylphenol, BH, obeyed eq II with a value of *q* equal to 2. Thus the inequality, $k_{11}(\mathrm{RO}_2\cdot) \gg k_{-9}(\mathrm{AH})$, utilized in the derivation of eq II is apparently valid and from this inequality we may calculate a minimum value of k_{11}, the rate constant for the reaction of an anthracenylperoxy radical with the 2,6-di-*t*-butyl-4-methylphenoxy radical. At AH equal to 0.87×10^{-4} M, RH equal to 0.196 M, and TPB equal to 0.31×10^{-3} M, the rate of oxygen absorption is 3.40×10^{-7} M sec^{-1} (*cf.* Table II). This rate is equal to $k_3(\mathrm{RO}_2\cdot)(\mathrm{RH}) + 2k_1(\mathrm{RR})$. Utilizing a value of k_3 equal to 350 M^{-1} sec^{-1},[8] the steady-state concentration of $\mathrm{RO}_2\cdot$ is cal-

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[8] Private communication to the authors by Dr. K. U. Ingold. At 30° in chlorobenzene the value of $k_3/(2k_4)^{1/2}$ equals 58.5×10^{-3} $M^{-1/2}$ sec$^{-1/2}$ and k_3 was found by the rotating sector technique to be 176 M^{-1} sec. The value of $k_3/(2k_4)^{1/2}$ equals 100×10^{-3} $M^{-1/2}$ sec$^{-1/2}$ at 60°. A reasonable assumption is that the difference in the value of the ratio is due primarily to the increase in the value of k_3.

culated to be equal to 6.2×10^{-9} *M*. Substitution of k_{-9}(AH) and the value for the concentration of $RO_2\cdot$ into the inequality places a lower limit on the value of k_{11} equal to 8.7×10^7 M^{-1} sec.

In Table V are summarized the values of other rate constants and ratios of constants which may be calculated from the results of this work and from the value of $2k_6/k_3k_8$ previously reported for 4-methoxyphenol.[2] The approximations utilized for the calculated quantities were that $(k_9/k_{-9})_{4\text{-}t\text{-butyl}} \cong (k_9/k_{-9})_{4\text{-methyl}} > (k_9/k_{-9})_{4\text{-H}}$ and that the value of k_6 for the reaction of the 4-methoxyphenoxy radical and the 9,10-dihydroanthracenylperoxy radical is equal to or smaller than 10^9 M^{-1} sec^{-1}.

Table V. Summary of Kinetic Parameters of the 4-Methoxyphenol-2,6-Di-*t*-butyl-4-Substituted Phenol Systems

Compound	Parameter	Value
2,6-Di-*t*-butyl-4-*t*-butyl	k_{10}/k_9	35.7–71.4
2,6-Di-*t*-butyl-4-methyl	k_{10}/k_9	67.0–134
2,6-Di-*t*-butyl-4-*t*-butyl	k_{10}/k_6	0.05
2,6-Di-*t*-butyl-4-methyl	k_{10}/k_6	0.1
2,6-Di-*t*-butyl-4-*t*-butyl	k_{10}	5.3×10^7 M^{-1} sec^{-1}
2,6-Di-*t*-butyl-4-methyl	k_{10}	1.0×10^8 M^{-1} sec^{-1}
4-Methoxyphenol	k_8	≤ 115 M^{-1} sec^{-1}
4-Methoxyphenol	k_7	$\leq 1.7 \times 10^7$ M^{-1} sec^{-1}
4-Methoxyphenol	k_5/k_{-5}	>50

The value for the partitioning of the 4-methoxyphenoxy radical between termination *via* reaction 10 and hydrogen abstraction from the hindered phenol, reaction 9, is consistent with the results of earlier studies of the 2,4,6-tri-*t*-butylphenoxy radical–nonhindered phenol systems.[3] In the earlier work it was demonstrated by the addition of excess 2,4,6-tri-*t*-butylphenol that $k_{10}/k_9 \geq 20$. A moderate steric effect is noted on the value of k_{10} since a decrease in the value of this constant is observed with increasing bulk of the 4 substituent.

The remaining entries in Table V yield information concerning the chemical reactivity of the 4-methoxyphenoxy radical. The calculated *upper* limit value for k_8 is approximately one-third as large as the value of k_3. This result is consistent with the high selectivity of the 4-methoxyphenoxy radical demonstrated in the previous paper of this series.[2] The results of earlier work from this laboratory suggested that the variation in the value of $k_6/2(k_4)^{1/2}(k_7)^{1/2}$, namely 49 for 4-methoxyphenol and 2.2 for phenol, was due primarily to changes in the value of k_7. In agreement with this view the *upper* limit value of k_7, the dimerization constant, for 4-methoxyphenol is two orders of magnitude smaller than the value of k_7 for the unsubstituted phenoxy radical.[9,10] The large sensitivity of the equilibrium constant k_5/k_{-5} to the structure of the phenol is demonstrated by the *lower* limit value of 50 for 4-methoxyphenol. The value of this constant for unsubstituted phenol is certainly less than 1.[11]

II. Inhibition Period and Quinol Ether Studies. The addition of 2,6-di-*t*-butylphenols at concentration levels where they have a small effect on the TPB-initiated oxidation of 9,10-dihydroanthracene has, however, a dramatic synergistic effect on the length of the inhibition periods produced by 4-methoxyphenol. A typical series of oxygen absorption *vs.* time curves are shown in Figure 3. Since the rate of radical production from TPB is accurately known, it is possible to determine the number of radical chains stopped during the inhibition period and thus to determine a stoichiometric factor, *n*,[12] defined as inhibitor + $n RO_2\cdot \rightarrow$ products for a single inhibitor or for a mixture of inhibitors.

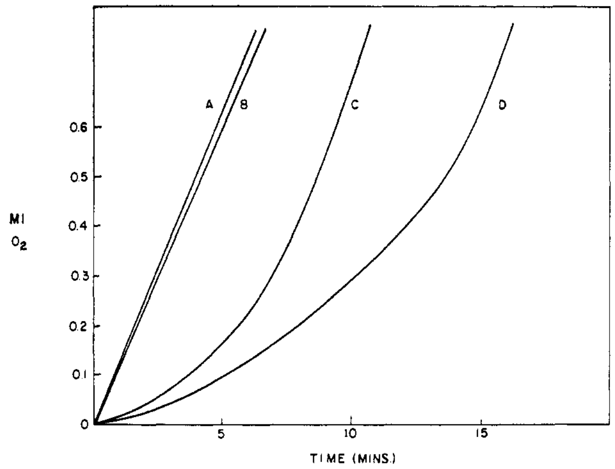
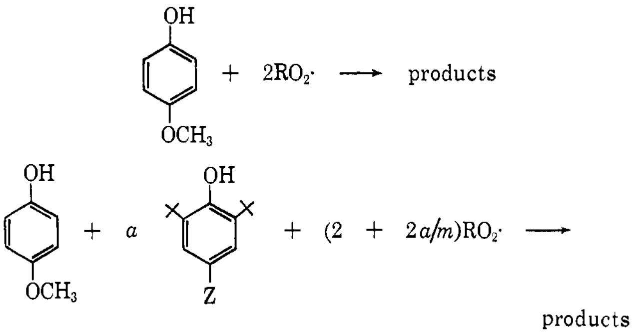


Figure 3. Inhibition periods with 4-methoxyphenol and 2,6-di-*t*-butyl-4-methylphenol. In all cases TPB equals 1.23×10^{-3} *M* and RH equal to 0.148 *M*: curve A, no additive; curve B, 1×10^{-4} *M* 2,6-di-*t*-butyl-4-methylphenol; curve C, 1×10^{-4} *M* 4-methoxyphenol; curve D, 1×10^{-4} *M* 2,6-di-*t*-butyl-4-methylphenol and 1×10^{-4} *M* 4-methoxyphenol.

The data obtained from a systematic variation of concentrations of 4-methoxyphenol and three hindered phenols are summarized in Table VI. The equations which best describe the stoichiometry associated with the reactions are



where *a* is the molar concentration of the hindered phenol and *m* is a number equal to 1.0 when Z is methyl or *t*-butyl, while $1 \leq m \leq 2$ when Z is hydrogen.

The stoichiometry observed for 2,6-di-*t*-butyl-4-methylphenol is in full accord with the results of the oxygen absorption study (γ less than 1), *i.e.*, the regeneration of 4-methoxyphenol *via* reaction 9 followed by the fast termination of the hindered phenoxy radical with peroxy radical, reaction 11. The less reactive 4-H compound also manifests behavior consistent with the results of oxidation studies. However, 2,4,6-tri-*t*-butylphenol exhibits the same stoichiometry as the 4-methyl compound, although the oxidation study suggested a complex and *mixed* termination *via* both reactions 10 and 11. This dichotomy could be resolved if

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[9] G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, **61**, 708 (1960).

[10] E. J. Land, G. Porter, and E. Strachen, *ibid.*, **59**, 2016 (1963).

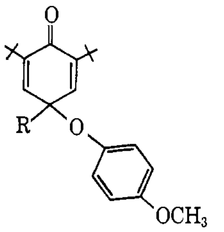
[11] J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 4807 (1964).

[12] C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 3233 (1955).

Table VI. Radicals Terminated by Mixtures of 4-Methoxyphenol and the Hindered Phenols

4-Methoxyphenol × 10^4 M	Concn-hindered phenol × 10^4 M	Radicals terminated × 10^4 M
1.0	...	2.29
2.0	...	4.59
3.0	...	6.14
	2,4,6-Tri-*t*-butylphenol	
1.0	1.0	4.10
2.0	1.0	6.61
3.0	1.0	8.46
1.0	2.0	5.95
2.0	2.0	8.46
3.0	2.0	10.28
	2,6-Di-*t*-butylphenol	
1.0	0.7	3.61
2.0	0.7	5.56
3.0	0.7	8.20
1.0	1.4	3.88
2.0	1.4	6.39
3.0	1.4	8.64
1.0	2.1	4.56
2.0	2.1	9.76
3.0	2.1	8.83
	2,6-Di-*t*-butyl-4-methylphenol	
1.0	1.0	5.08
2.0	1.0	7.3
3.0	1.0	10.7
1.0	2.0	6.62
2.0	2.0	10.6
3.0	2.0	11.9
0.0143	1.02	2.00
0.307	1.02	3.08
0.714	1.02	3.86

the product of reaction 10, Ia, functions as an inhibitor with a stoichiometric factor equal to 2.



Ia, R = *t*-butyl
b, R = methyl

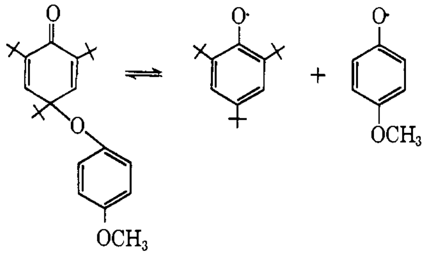
The compound was prepared and tested as an inhibitor. Well-defined inhibition periods were obtained (Figure 4), and the results summarized in Table VII demonstrate that the compound has the correct stoichiometric factor.

Table VII. Radicals Terminated by Mixtures of Ia and 2,4,6-Tri-*t*-butylphenol

Dienone × 10^4 M	Concn-hindered phenol × 10^4 M	Radicals terminated × 10^4 M
1.05	...	2.0
1.57	...	3.10
2.10	...	4.34
	2,4,6-Tri-*t*-butylphenol	
0.7	1.0	3.34
1.4	1.0	5.52
2.1	1.0	6.39
0.5	2.0	5.08
1.0	2.0	5.96
1.5	2.0	6.84
2.0	2.0	7.88

The quinol ether is a unique inhibitor since it does not contain a readily abstractable hydrogen as do conventional antioxidants. Recent investigations of related systems suggest that the –CO– ether bonds of such compounds are relatively weak. For example, the oxidative coupling of 2,6-xylenol apparently involves the equilibration of unstable quinol ether intermediates.[13] The reports of Coppinger[14] on the presence of two radicals in a solution of oxygen and the 2,4,6-tri-*t*-butylphenoxy radical and the thermal stability of other quinol ethers reported by Müller, *et al.*,[15] also suggest that such bonds are prone to thermal scission.

An attractive hypothesis for the inhibitory effect of this compound involves an equilibrium reaction with its precursors, *i.e.*



The occurrence of this equilibrium would result in a complex expression for the oxidation rates. Although a low steady-state concentration of radicals would be established and termination would occur with peroxy radicals *via* reactions 6 and 11, the restarting of chains by the 4-methoxyphenoxy radical would also occur. A number of ancillary experiments support this interpretation. The addition of 2,4,6-tri-*t*-butylphenol leads to a pronounced increase in the length of the inhibition period manifested by the quinol ether (*cf.* Table VIII). This synergistic effect could occur *via* the hydrogen transfer reaction 9. Further evidence for radical formation from the quinol ether is found in its behavior in the presence of 2,6-di-*t*-butyl-4-methylphenol. The quinol ether was quantitatively recovered after refluxing in benzene for 3 days. However, after 6 hr reflux in the presence of 2,6-di-*t*-butyl-4-methylphenol and evaporation of the solution to dryness, 3,3′,5,5′-tetra-*t*-butylstilbene-4,4′-quinone was produced. The precursor of the stilbenequinone is the 2,6-di-*t*-butyl-4-methylphenoxy radical.[16] Finally, at concentrations less than 2 × 10^{-3} M the quinol ether is a strong inhibitor while at higher concentrations it functions as an initiator for the oxidation of 9,10-dihydroanthracene. For example, in the absence of TPB and at 10.5 × 10^{-3} M quinol ether, the oxidation rate with 99 × 10^{-3} M 9,10-dihydroanthracene is equal to 7.2 × 10^{-7} M $\sec^{-1}$. The quinol ether does not itself absorb oxygen at a measurable rate since the rate of oxygen absorption in the presence of TPB and in the absence of hydrocarbon corresponds to the known rate of decomposition of TPB.

The product of the reaction of 4-methoxyphenoxy and 2,6-di-*t*-butyl-4-methylphenoxy radicals would be the quinol ether Ib. Although this compound is unknown a study of the products of the oxidation of

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(13) G. D. Cooper, H. S. Blanchard, G. F. Endes, and H. Finkbeiner, *J. Am. Chem. Soc.*, **87**, 3996 (1965).

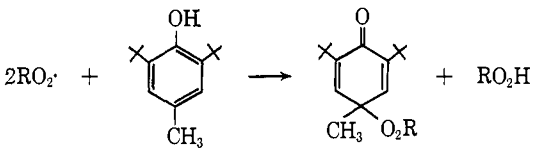
(14) G. M. Coppinger, *ibid.*, **86**, 4385 (1964).

(15) E. Müller, K. Ley, and G. Schlechte, *Ber.*, **90**, 2660 (1957).

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

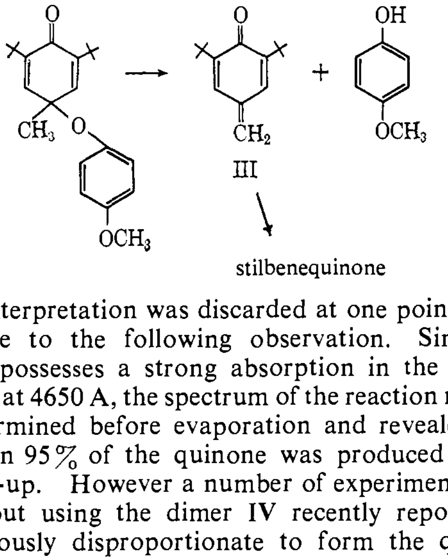
2,6-di-*t*-butyl-4-methylphenol in the presence of 4-methoxyphenol where it is presumably generated as an intermediate was carried out.

The oxidation of 2,6-di-*t*-butyl-4-methylphenol by the decomposition of TPB in oxygen-saturated solution gave a high yield of 1-methyl-(1-peroxy-1,1-diphenylethane)-3,5-di-*t*-butyl-2,5-cyclohexadien-4-one (II) as reported by earlier workers.[17]

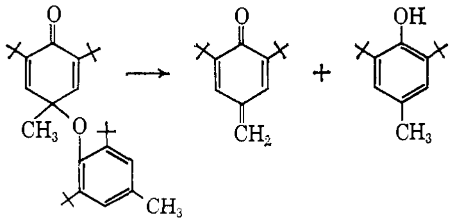


II

In contrast the decomposition of TPB in the presence of mixtures of 2,6-di-*t*-butyl-4-methylphenol and 4-methoxyphenol yielded on evaporation of the reaction solution an orange solid containing 3,3′,5,5′-tetra-*t*-butylstilbene-4,4′-quinone. The compound was identified by thin layer chromatography and the amount of quinone (1 mole of quinone/10 moles of peroxy radicals produced in the system) was determined by visible absorption spectroscopy. Compound II is not converted to the quinone in the presence of 4-methoxyphenol since it is stable in its presence for 16 hr at 60°. The precursor of the quinone has been reported to be the quinone methide (III). This compound may be produced in our system from the decomposition of a quinol ether intermediate Ib, *i.e.*



This interpretation was discarded at one point of the work due to the following observation. Since the quinone possesses a strong absorption in the visible, ε 9 × 10^4 at 4650 A, the spectrum of the reaction mixture was determined before evaporation and revealed that more than 95% of the quinone was produced during the work-up. However a number of experiments were carried out using the dimer IV recently reported to spontaneously disproportionate to form the quinone methide and the parent phenol, *i.e.*[18]



IV

Solutions of 2.8 × 10^{-5} *M* and 2.66 × 10^{-3} *M* IV were prepared in isooctane. The dilute solution exhibited a strong absorption at 2850 A with ε 2.6 × 10^4 which has previously been attributed to III.[18,19] The absorption spectra of the concentrated solution indicated that less than 0.003 × 10^{-3} *M* stilbenequinone was present. The same results with both solutions were obtained after 17 hr at room temperature. Evaporation of the diluted solution to dryness and redilution with isooctane resulted in a solution which gave an absorption spectra identical with 0.055 × 10^{-5} *M* stilbenequinone.

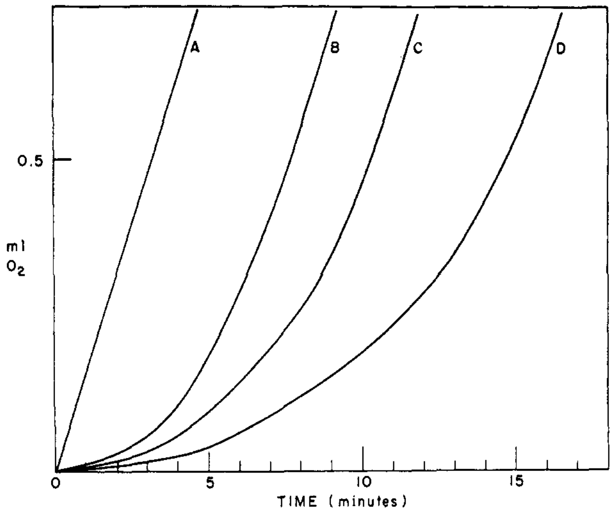


Figure 4. Inhibition period with quinol ether. In all cases TPB equals 1.23 × 10^{-3} *M* and RH equals 0.148 *M*: curve A, no additive; curve B, 1 × 10^{-4} *M*; curve C, 1.57 × 10^{-4} *M*; curve D, 2.1 × 10^{-4} *M*.

A solution of the dimer (2.66 × 10^{-3} *M* in chlorobenzene) also revealed that less than 0.003 × 10^{-3} *M* quinone was present. However, on evaporation to dryness and redilution a spectrum identical with 0.0815 × 10^{-3} *M* quinone was obtained. These results are consistent with the view that in isooctane and in chlorobenzene at 2.66 × 10^{-3} *M* the quinone methide is stable and is converted to the stilbenequinone only on work-up under our experimental conditions.

Relation of Present Work to the General Phenomena of Synergism. An examination of the literature[20–22] in which synergism has been reported reveals that effective combinations of phenolic inhibitors frequently consist of a mixture of a hindered phenol substituted with at least one *t*-butyl group at the *ortho* position and a nonhindered phenol. Ingold[23] reported the effect on the length of the induction periods of the autoxidation of a saturated mineral oil at 160° protected by mixtures of antioxidants. From his results he suggested that "synergism results mainly from one inhibitor functioning as a peroxide decomposer and the other as a free radical trap, although the correlation between the magnitude of the synergistic effects and the relative rates of peroxide decomposition is rather poor."[23] Since the initiation of radical chains in the system utilized in the present study is not due to hydroperoxide decomposi-

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(17) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).
(18) H. D. Becker, *J. Org. Chem.*, 30, 982 (1965).
(19) L. J. Filar and S. Winstein, *Tetrahedron Letters*, 9 (1960).
(20) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).
(21) J. R. Chipault in "Autoxidation and Antioxidants," Vol. II, W. O. Lindberg, Ed., Interscience Publishers, Division of John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 12.
(22) G. Scott, "Atmospheric Oxidation and Antioxidant," Elsevier Publishing Co., New York, N. Y., 1965, p 205.
(23) K. U. Ingold, *J. Inst. Petrol.*, 117, 375 (1961).

tion, one must conclude that a hydroperoxide decomposer is not a necessary component for a synergistic combination.

A mechanism which gives a good account for the synergistic effects observed with such mixtures is based on the sequence of reactions developed in the present work. In practice the autoxidation of a hydrocarbon is autocatalytic; that is, the decomposition of the product hydroperoxide initiates free-radical chains in the system. The ability of an antioxidant to fully suppress reaction 3 is then of prime importance in the determination of the length of the inhibition period which is obtained by its use. Although the value of k_5/k_3 may not be large for a hindered phenol, BH, the formation of hydroperoxide *via* reaction 3 in such a system may be completely suppressed by the addition of a sufficiently large quantity of BH. In contrast, the addition of unlimited amounts of a nonhindered phenol, AH, with a large value for k_5/k_3 cannot fully suppress the formation of hydroperoxide due to chain restarting reactions -5 and 8. Upon the addition of BH, reactions -5 and 8 are unable to compete with reaction 9 and reaction 7 is superceded by reactions 10 and/or 11. The rate of formation of the hydroperoxide is greatly reduced, the length of the inhibitor period is increased, and the mixture is said to be synergistic.

The magnitude of the synergistic effect observed with such mixtures depends upon several kinetic parameters, the most important of which is the rate of regeneration of the nonhindered phenol, reaction 9, compared to the rate of the chain restarting reactions -5 and 8. This quantity, k_9/k_{-5}, may be obtained by study of the oxidation rate of the individual compounds and studies involving the 2,4,6-tri-*t*-butylphenoxy radical as outlined above. The values of k_9/k_{-5} for 4-*t*-butylphenol[24] and 4-methoxyphenol are 100 and 370–750. The amount of synergism reported by Ingold for 4-methylphenol and 4-methoxyphenol are 5 and 45 min, respectively. The nonhindered phenol which Ingold reported to manifest the strongest synergistic behavior (160 min) was 2,4,6-trimethylphenol. We have not been able to measure the rate of reaction -9 for this compound, but in analogy with the previous result obtained with nonhindered phenols the value of k_9/k_{-5} for this compound should be somewhat larger than that obtained for 4-methoxyphenol.[25] Compounds which failed to manifest a significant synergistic effect with 2,6-di-*t*-butyl-4-methylphenol are those which do not restart chains *via* reactions -5 and 8,[1] namely, 1-hydroxynaphthalene and 2,4,6-tri-*t*-butylphenol.

Several independent lines of evidence also support this mechanism. It has been reported that the nonhindered phenol component of effective synergistic combinations frequently has an optimum concentration[22] as is observed with 4-methoxyphenol in the present study. In addition the most effective hindered phenol component is 2,6-di-*t*-butyl-4-methylphenol also consistent with the findings in this work. An extension of the mechanism to account for the so-called antagonistic effects observed with mixtures of nonhindered phenolic compounds is possible. The facile equilibria of phenoxy radicals to yield phenoxy radicals of varying degrees of reactivity toward chain restarting reactions and the occurrence of favored cross-termination reactions can lead to such effects.

Experimental Section

Materials. The oxidizable hydrocarbon 9,10-dihydroanthracene was obtained from Henley and Co. (98% minimum). This material, after three recrystallizations from ethanol, had a mp 109.5–110.0° cor (lit.[8] 109–110.5°). Periodically during use the hydrocarbon was subjected to iodometric analysis and contained less than 0.02% (limit of detection) hydroperoxide. Spectrophotometric analysis revealed an impurity of 0.08% anthracene.

2,2,3,3-Tetraphenylbutane was synthesized by the method of Müller and Roscheisen,[26] mp 122–123° (lit.[26] 122–123°).

9,10-Dihydro-9-anthryl hydroperoxide was prepared according to the procedure of Bickel and Kooyman.[17] Two recrystallizations from toluene–pentane yielded a material of mp 109–110°; iodometric analysis gave a value of 95% peroxide. The material contained a 4.8% impurity of anthracene as determined by spectrophotometric analysis.

4-Methoxyphenol was Eastman reagent grade. The material was recrystallized from methyl alcohol, mp 58–59°. The purity of the material was also determined by thin layer chromatography on silica gel plates. The material yielded one spot on elution with benzene followed by a 20% chloroform–benzene mixture.

The hindered phenols were obtained from commercial sources and purified by recrystallization to yield materials whose melting points agreed with literature values. The purity of the compounds was also determined by glpc and tlc. The materials yield a single peak on the gas chromatograph and a single spot on the thin layer silica gel plate.

4-(4-Methoxyphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-2-one was prepared *via* the DDQ adduct as previously described in the literature,[27] mp 78.5–79.5°.

3,3′,5,5′-Tetra-*t*-butylstilbene-4,4′-quinone[27] was prepared by reaction of 2,6-di-*t*-butyl-4-methylphenol with DDQ. Recrystallization from benzene–ethyl alcohol yields red needles, mp 313°.

4-(2,6-Di-*t*-butyl-4-methylphenoxy)-2,6-di-*t*-butyl-4-methyl-2,5-cyclohexadien-1-one (IV) was prepared according to procedure of Becker.[18]

Induction Periods. The induction periods were measured in the oxygen absorption apparatus previously described.[28] The end of the induction period was chosen as that point at which the rate of oxygen absorption was the same as the uninhibited rate, correction being made for the consumption of initiator. The total number of radicals stopped by the phenol was calculated from the first-order rate constant for the decomposition of 2,2,3,3-tetraphenylbutane.

Rate Measurements. All the rate measurements reported in this work were determined on the automatic constant-pressure apparatus recently developed in this laboratory.[29]

Product Studies of 2,6-Di-*t*-butyl-4-methylphenol in the Absence and in the Presence of 4-Methoxyphenol. a. A mixture of 31.4 mg (0.146 mmole) of 2,6-di-*t*-butyl-4-methylphenol and 40 mg (0.110 mmole) of 2,2,3,3-tetraphenylbutane in 10 ml of chlorobenzene was stirred under oxygen at 60.0° for 16 hr. The solvent was evaporated under reduced pressure at room temperature, and the colorless solid residue was dissolved in 5 ml of chloroform and subjected to infrared analysis. The solution exhibited strong absorptions at 6.00 and 6.10 μ. Employing a value of ϵ equal to 280 l. mole^{-1} cm^{-1} at 6.00 μ obtained from pure compound, the total amount of dienone formed in the reaction was determined to be 0.11 mmole.

b. The above reaction was duplicated. At the end of the 16-hr period 29 mg (0.234 mmole) of 4-methoxyphenol was added, and the solution was stirred for an additional 16 hr at 60°. Stilbenequinone was shown to be absent from the white solids isolated in cases a and b by both visible absorption spectra and by tlc analysis with samples of the pure stilbenequinone.

c. A solution of 30 mg (42.8 mmoles) of TPB, 29.0 mg (234.0 mmoles) of 4-methoxyphenol, and 40.6 mg (188 mmoles) of 2,6-di-*t*-butyl-4-methylphenol in 10 ml of chlorobenzene was stirred

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[24] The effects of *t*-butyl and methyl group at the 4 position for reactions 9 and 5 should be equivalent.

[25] A plot of the log of k_{-9} (24° in benzene) *vs.* log k_6/k_3 (60° in chlorobenzene) for a number of substituted nonhindered phenols yields a line of slope *ca.* 2.0. The extrapolated value of k_{-9} for 2,4,6-trimethylphenol is 2.5 × 10^4 M^{-1} sec^{-1}, and the value of k_9/k_5 lies in the range 780–1560.

[26] E. Müller and G. Roscheisen, *Ber.*, **90**, 543 (1957).

[27] H. D. Becker, *J. Org. Chem.*, **29**, 3068 (1964).

[28] L. R. Mahoney, *J. Am. Chem. Soc.*, **86**, 444 (1964).

[29] L. R. Mahoney, R. W. Bayma, A. Warnick, and C. H. Ruof, *Anal. Chem.*, **36**, 2516 (1964).

under oxygen at 60° for 16 hr. The visible absorption spectra revealed that less than 0.03 × 10^{-3} mmole of stilbenequinone was present in the sample. On evaporation to dryness at room temperature an orange solid was obtained. This solid on dissolution in chlorobenzene yielded an absorption spectra which corresponded to the presence of 4.54 × 10^{-3} mmole of the stilbenequinone present in the original sample. A spot identical with that obtained from a pure sample of the stilbenequinone was also observed on a tlc plate.

Reaction of Ia with a 2,6-Di-*t*-butyl-4-Methylphenol. A mixture of 102.6 mg (0.27 mmole) of 4-(4-methoxyphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one and 80.8 mg (0.38 mmole) of 2,6-di-*t*-butyl-4-methylphenol in 50 cc of benzene was refluxed 6 hr. The solvent was removed under reduced pressure and the residue taken up in an appropriate volume of chloroform and analyzed by infrared utilizing the absorbance at 6.26 μ. Analysis shows 36.4 mg (0.084 mmole) of quinone. A spot identical with that obtained from a pure sample of stilbenequinone was observed on a tlc plate.

Acknowledgment. The authors acknowledge the expert technical assistance rendered by Mrs. L. Skewes, Miss I. Golebiewska, and Mr. F. Ferris.

Photochemical Transformations of an *o*-Vinylbenzophenone

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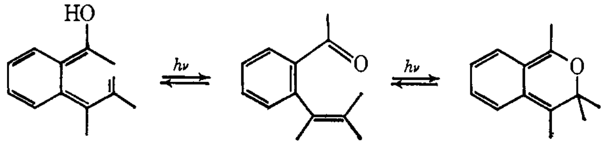
Received June 7, 1967

Abstract: 2-(2-Methyl-1-phenylpropenyl)benzophenone (V) has been found to be photochromic at low temperatures. The colored species, which appears to be the valence tautomer VI, could be trapped as a Diels–Alder adduct with tetracyanoethylene. Prolonged ultraviolet irradiation of V in benzene afforded 1,1-dimethyl-2,3-diphenyl-2,3-epoxyindan (VIII), while in methanol 4,4-dimethyl-1,3-diphenyl-1-methoxyisochroman (X) was formed. The nature of the possible intermediates involved in the formation of VIII and X is discussed.

While the photolyses of a number of γ,δ-unsaturated ketones have been shown to give bicyclic oxetanes,[1,2] the photochemistry of simple aliphatic α,β,γ,δ-unsaturated ketones is complicated by light-induced polymerization.[3] However, on incorporation of the γ,δ double bond into a ring such as in β-ionone,[3,4] a photochemical ring-chain tautomerization can be established between the *cis*-dienone and a 2H-pyran.[5] As part of a study of photochromism, an investigation of a related system containing an *o*-vinylphenone moiety (I) seemed of interest. A transformation of this compound analogous to the dienone–pyran interconversion could be envisioned in which irradiation of I might generate the colored quinonoidal structure (II), which might then undergo thermal reconversion to I in the dark.[6] Alternatively, if I contained suitably situated alkyl groups, a reversible photoenolization (I ⇄ III) might take place in analogy to the photochemical reactions of *o*-alkylbenzophenones.[7]



III I II

Results

The compound chosen for study was the known 2-(2-methyl-1-phenylpropenyl)benzophenone (V),[8] prepared by acid-catalyzed ring opening of 1,3-dihydroxy-2,2-dimethyl-1,3-diphenylindan (IV). While exposure of colorless solutions of V to high intensity ultraviolet light affected no visible changes at room temperature, at −78° in ethyl acetate, acetone, methylene chloride, or isopropyl alcohol a moderately intense orange color developed. The color faded slowly in the dark at −78° (∼30 min) but the rate increased greatly at higher temperatures, and the color completely faded upon allowing the solution to warm to approximately −40°. A more intense coloration was obtained by irradiation of an ethanol–ether glass containing V at −196°. Rapid photobleaching occurred upon exposure of the colored solutions or glass to strong visible light.

Qualitative observations on the effect of certain additives on the colored species provided no support for a photoenol structure such as III but were consistent with the assignment of the 2H-pyran structure VI to the colored species. Thus, no noticeable change in the intensity, color, or fading rate was observed when V was irradiated at −78° in the presence of small amounts of trifluoroacetic acid, triethylamine, or dilute aqueous sodium hydroxide. Since these reagents would all be expected to affect the stability or color of a photoenol, this structure can be safely eliminated. On the other hand, color formation was completely suppressed in the presence of tetracyanoethylene (TCNE), and addition of this reagent to a preformed orange solution resulted in the immediate discharge of the color. This behavior was consistent with the

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(1) R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960).

(2) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Letters*, 1525 (1965).

(3) G. Buchi and N. C. Yang, *J. Am. Chem. Soc.*, **79**, 2318 (1957).

(4) P. de Mayo, J. B. Stothers, and R. W. Yip, *Can. J. Chem.*, **39**, 2135 (1961).

(5) E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *J. Am. Chem. Soc.*, **88**, 619 (1966).

(6) For a related photochromic system in which the color changes are the inverse, see R. S. Becker and J. Michl, *ibid.*, **88**, 5931 (1966).

(7) (a) N. C. Yang and C. Rivas, *ibid.*, **83**, 2213 (1961); (b) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963); (c) E. F. Ullman and K. R. Huffman, *Tetrahedron Letters*, 1863 (1965); (d) K. R. Huffman, M. Loy, and E. F. Ullman, *J. Am. Chem. Soc.*, **87**, 5417 (1965).

(8) F. V. Brutcher and H. J. Cenci, *J. Org. Chem.*, **21**, 1543 (1956).