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CHEMISTRY OF HINDERED PHENOLS

REACTIVITY OF 2,6-Di-t-BUTYL-4-METHYLPHENOXYL

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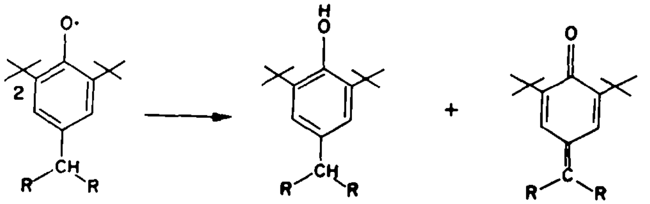
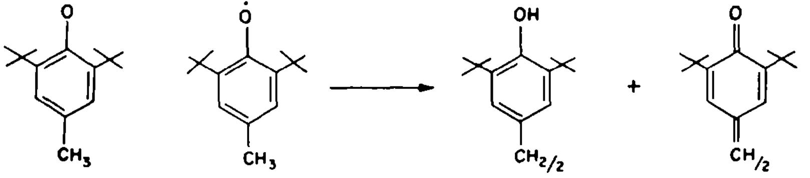
Abstract—The phenoxy free radical, 2,6-di-t-butyl-4-methylphenoxyl, reacts with itself to form 3,5-di-t-butyl-4,1-quinonemethide and 2,6-di-t-butyl-4-methylphenol in equivalent amounts. The quinone-methide reacts with itself through the formation of free radical intermediates to form 1,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)ethane and 3,3',5,5'-tetra-t-butylstilbene-4,4'-quinone.

INTRODUCTION

Phenoxyl free radicals from the generic class of hindered phenols possess sufficient stability to permit confirmation of their existence and examination of their structure. The investigations of Cook *et al.*[1] and of Müller *et al.*[2] have demonstrated clearly that free radical decay occurs by the path:



The rate of free radical disappearance is second order in free radical (I) and the products are the parent phenol and a quinone methide.[1,2] There is, however, an apparent exception to these general observations:



The rate decay of IV is too fast to measure[1] but the products that have been reported are not those in Eq (1) but rather those in Eq (2).

This difference has been attributed to the rearrangement of IV dimerization of VIII to form VI and subsequent oxidation by whatever means to VII.[3]

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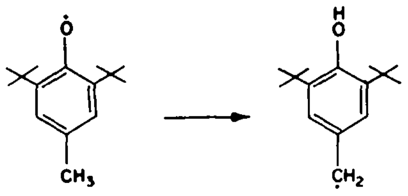
[1] C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.* **81**, 1176 (1959); **78**, 3797 (1956).

[2] E. Müller, R. Mayer, U. Heilmann, and K. Scheffler, *Liebigs Ann.* **645**, 66 (1961).

[3] C. D. Cook, N. G. Nash, and H. R. Flanagan, *J. Amer. Chem. Soc.* **77**, 1783 (1955).



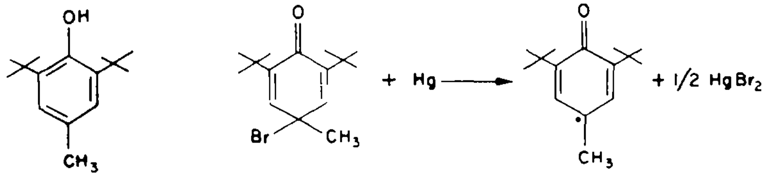
IV VIII (3)

In the discussion following we will attempt to show that this rearrangement is not necessary to account for dimeric products and that the reactivity of the phenoxy free radical IV conforms to that of other hindered phenols.

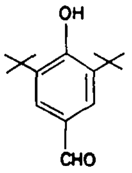
RESULTS AND DISCUSSION

The differences reported in the decay of the phenoxy radical IV when compared with others of the generic class consists in observation of dimer products.

Cook *et al.*[3] isolated the products IX, VI and VII in the mole ratios of 3·7:0·8:1. Using a somewhat different analytical procedure we were also able to establish the ratio of products IX, VI and VII is indeed 4:1:1. The free radical IV was generated in t-butyl alcohol under nitrogen according to reaction[1] (4). Under these conditions no oxidation of the free radical occurs from other sources so that products reflect only the reactivity of phenoxy free radical.* The stilbenequinone VII was rather easily isolated by virtue of its limited solubility. After this separation had been made, the remaining solution was treated with bromine. The products were additional VII and 3,5-di-t-butyl-4-hydroxybenzaldehyde (V). The stilbenequinone was the product of the oxidation of the bisphenol VI, but V was clearly derived from the parent phenol IX[4] since neither VI nor VII, the stilbenequinone, yielded any aldehyde on treatment with bromine.



IX X IV (4)



V

It was possible in this way to determine that in this sequence, reaction 4 followed by bromination, the mole ratio of the parent phenol IX to total stilbenequinone VII

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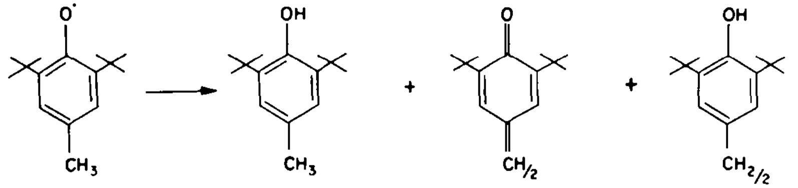
* A variety of free radicals of the generic class have been prepared in this way and the presence of Hg and $HgBr_2$ has had no effect on the system.

[4] G. M. Coppinger and T. W. Campbell, *J. Amer. Chem. Soc.* **75**, 734 (1953).

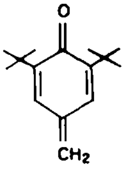
was 2. The mole ratio of IX to VII in the bromination step only was 4. Since it was apparent that the stilbene-quinone VII observed was obtained by bromination of the corresponding phenol VI, the reaction of the phenoxy free radical is the following:



IV IX VII VI (5)

and the products are in the ratios of 4 : 1 : 1.

The remaining difference between this special case and the generic class is the failure to observe a quinone methide as a product. This is readily explained in terms of the enhanced reactivity of this quinone methide when compared with homologs.



XI

The compound XI reacts with itself in inert solvent to form the dimeric compounds VI and VII in equal amounts.[5] It was further possible to demonstrate that XI is an intermediate in reaction (5) by following the course of the reaction in very dilute solution in isooctane by means of a U.V. spectrometer. Under these conditions, the concentration of the quinone methide was so low that no dimerization occurred. Measurement of the principal band at 2850 A, ε, 30,500 l m^{-1} cm^{-1},[6]* indicated that the quinone methide accounted for 50 per cent of the phenoxy free radical formed (see Fig. 1). Neither the bromocyclohexadienone X nor the other product, the parent phenol IX, interfered with this measurement; the adsorptivity of the phenol is lower by more than one order of magnitude at 2850 A and a window exists in the quinone methide spectrum at the position of maximum adsorption of X, 2480 A. The time scale in Fig. 1 is 0–2 hr.

It seems clear from these observations that the general reaction (1) applies to decay of the phenoxy free radical IV and that the peculiar distribution of products reflect the reactivity of the quinone methide produced and not the character of the phenoxy radical. In particular, it is not necessary to employ a rearrangement argument suggested by reaction (3) for which there is no experimental evidence.

The reaction of the quinone methide XI to form the dimeric products VI and VII has unique properties which are not yet clearly understood. It is a reaction which produces intermediate free radicals.

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* Reference spectrum of the quinonemethide was obtained by dehydrobrominating 4-bromomethyl-2,6-di-t-butylphenol with an equal molar quantity of tripropylamine in isooctane.

[5] L. J. Filar and S. Winstein, *Tetrahedron Letters* No. 25, 9 (1960).

[6] R. H. Bauer and G. M. Coppinger. Unpublished.

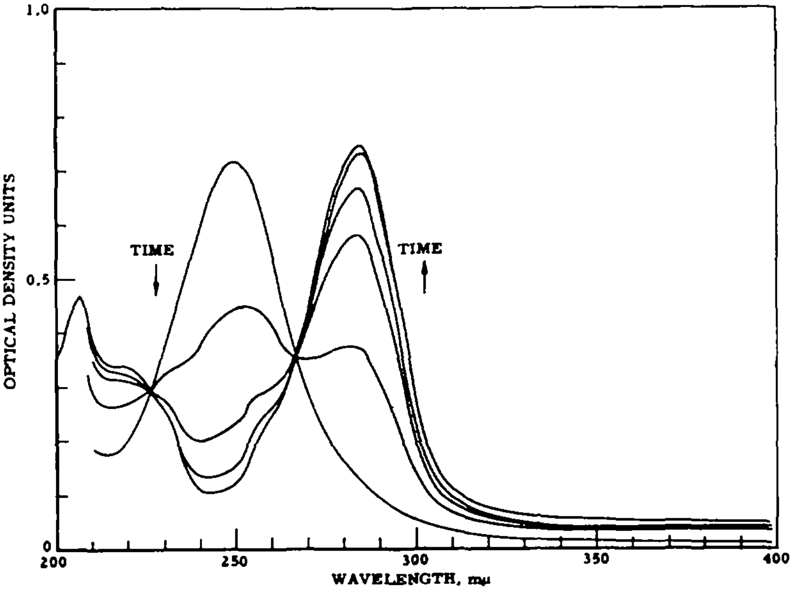


FIG. 1. Reaction of 2,6-di-t-butyl, 4-bromo, 4-methylcyclohexa-3,5-dienone with mercury ultra violet spectrum

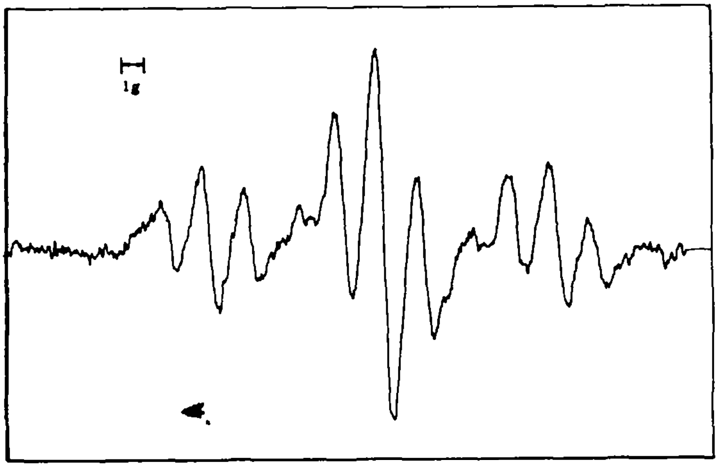
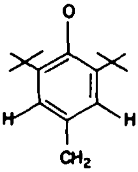
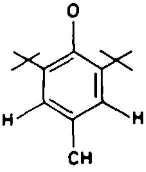


FIG. 2. 3,5-Di-t-butyl-*p*-quinonemethide in isooctane solution
1st Derivative, E.P.R. spectrum

When the quinone methide (XI) prepared by reaction (4) was allowed to react with itself in isooctane solution in the cavity of an electron paramagnetic resonance spectrometer the spectra of free radicals was observed, Figs. 1 and 2. These were resolved by an arithmetic interpolation method into two distinct spectra, one of three sets of triplets and one of two sets of triplets. The former is characteristic of the partial structure XII with hyperfine splitting of each of two pairs of hydrogens to account for the three triplets: the latter is characteristic of the partial structure XIII with hyperfine splitting assigned in the same way.[7] The splitting observed were[7]



XII



XIII

XII $A_{H\,ring}$ 2·10 g, $A_{H\,benzyl}$ 10·5 g; XIII $A_{H\,ring}$ 1·94 g, $A_{H\,benzyl}$ 8·05 g.

It has not been possible to draw any conclusions regarding the nature of the missing fragments nor to suggest the initial course of the reaction of the quinone methide. It is unlikely that a singlet-triplet transition of the quinone methide occurs since the reaction does not require light. A more reasonable alternative is that a bimolecular reaction occurs which forms two free radical species perhaps in the nature of a charge transfer pair with electron exchange forces holding the pair together until carbon–carbon bond formation occurs.

Either of these processes is necessarily followed by disproportionation of the free radicals to form the stable products. Whatever the nature of the initial interaction, the simplicity of the products implies that the reactivity of the intermediate free radicals is specific and that no branching occurs.

CONCLUSIONS

The reactivity of the phenoxy free radical 2,6-di-t-butyl-4-methylphenoxy conforms to the general pattern of the hindered phenol generic type. It reacts by a bimolecular path to form 2,6-di-t-butyl-4-methylphenol and 3,5-di-t-butyl-*p*-quinonemethide in equal quantities.

The quinone methide reacts with itself through formation of intermediate free radicals to yield in equal amounts 1,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)ethane and 3,3′,5,5′-tetra-t-butyl-4,4′-stilbenequinone.

EXPERIMENTAL

2,6-Di-t-butyl-4-methylphenol was recrystallized from isooctane, mp 69–69·5°.

2,6-Di-t-butyl-4-bromo-4-methylcyclohexa-3,5-dienone (X) was prepared by bromination of 2,6-di-t-butyl-4-methylphenol in wet acetic acid[4] and recrystallized from isooctane, mp 90–91°, yield 51 %.

Reaction of 2,6-*di-t-butyl-4-bromo-4-methylcylcohexa*-3,5-*dienone* (X) *with mercury.* To a solution of 10 g (X) in 500 cc t-butyl alcohol under nitrogen was added 20 g mercury. The mixture was stirred at room temp for 4 hr. The mixture was filtered free of mercuric bromide and mercury. Upon dilution with water, 3,3′,5,5′-tetra-t-butyl stilbene-4,4′-quinone (VII) precipitated. This was filtered and washed with wet t-butyl alcohol, yield 1·5 g, mp 310–315°. The compound was recrystallized from benzene, mp 316°.

The remaining solution after isolation of the stilbene-quinone was treated with 4·0 cc bromine at room temp. Thiosulfate solution was added to destroy residual bromine and the total product was isolated by precipitation with water and filtration. The total product was suspended in an

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[7] J. K. Becconsall, S. Clough and G. Scott, *Trans. Faraday Soc.* **56**, 459 (1960); *Proc. Chem. Soc.* 308 (1959).

aqueous sodium carbonate solution and heated. The stilbene-quinone was removed by filtration and washed with hot sodium carbonate solution, yield 1·9 g, mp 312–315°.

The carbonate solution was acidified with HCl to afford 3,5-di-t-butyl-4-hydroxybenzaldehyde (V), yield 3·5 g, mp 188–190°.

With the assumption that the precursors of the stilbene-quinone obtained in the bromination was 1,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)ethane, (VI) and of the aldehyde, 2,6-di-t-butyl-4-methylphenol (IX), the distribution of the 3 products from the phenoxy free radical were 21 %, 26 % and 45 %, respectively, with the conversion of the bromocyclohexadienone at 100 %.

Reaction of 1,2-*bis*(3,5-*di-t-butyl*-4-*hydroxyphenyl*)-*ethane* (VI) *with bromine.* A solution of 2·0 g bisphenol (VI) in 100 cc t-butanol was treated with 2 cc bromine at room temp. The stilbene-quinone (VII) was precipitated by addition of water and recrystallized from benzene, yield 1·6 g, mp 314°.

This same sequence of reactions was examined spectroscopically by taking aliquot portions before and after bromination, removing the solvent *in vacuo* and examining chloroform solutions in the infrared. The yield of VII was determined by measurement of the absorption band at 6·35 μ and the aldehyde (V) by use of the band at 5·95 μ. The measurements led to the conclusion that the respective yields based upon the bromocyclohexadienone were 23 % and 46 %, respectively.

The reaction of the bromocyclohexadienone X and mercury in isooctane solution, 5·6 × 10^{-5} M, was followed by measurement of the U.V. spectra with a Cary model 15 spectrometer. The results are shown in Fig. 1. The maximum absorptivity at 2850 A assigned to the quinone methide XI occurred at the end of 2 hr and remained unchanged after a further 2 hr. The band at 2480 A is characteristic of the bromo-cyclohexadienone (X).

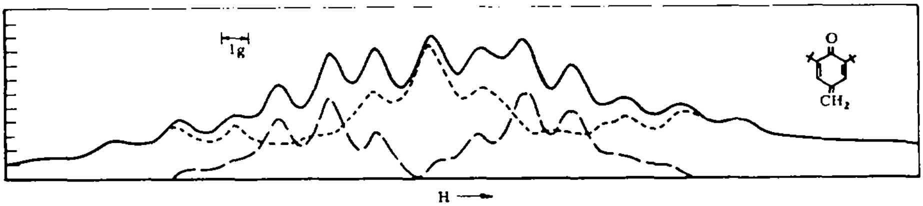

FIG. 3. 3,5-Di-t-butyl-*p*-quinone methide in isooctane solution
Absorption E.P.R. spectrum

The electron paramagnetic resonance spectrum, Fig. 2, was obtained using a Varian V-4500 spectrometer utilizing 100 kc modulation. The upper trace of Fig. 3 is the experimental curve which was resolved into the two lower curves by a method of arithmetic interpolation. The measurements were made in isooctane under vacuum. The concentration of free radical species was approximately 10^{-3} molar. The initial quinone-methide concentration was approximately 10^{-2} molar.