ethanol gave the analytical sample: mp 203.5–205°; λ_{max} 295, 328 mμ; ν 1695, 3230 cm^{-1}.

Anal. Calcd for $C_{19}H_{21}NO_6S$: C, 58.29; H, 5.41; N, 3.58; S, 8.20. Found: C, 58.36; H, 5.51; N, 3.43; S, 8.42.

N-Formyl-1-carbethoxymethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IId).—Compound IIa (27.93 g) was mixed with 350 ml of ethyl formate and heated under reflux for 1 hr. Removal of the solvent under reduced pressure left the N-formyl derivative as a yellow oil which readily crystallized. Trituration with ether gave a pale yellow solid (28.03 g, 91%), mp 104–107°. The colorless analytical sample, obtained by recrystallization from ether, had mp 107.5–108°; λ_{max} 285 mμ; ν 1725, 1655 cm^{-1}.

Anal. Calcd for $C_{16}H_{21}NO_5$: C, 62.52; H, 6.88; N, 4.56. Found: C, 62.55; H, 6.97; N, 4.53.

N-Formyl-1-carboxymethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IIe).—To a solution of IId (10 g) in 75 ml of 50% aqueous ethanol was added 7.5 g of potassium hydroxide, and the solution was refluxed for 30 min. The solution was cooled, diluted with 200 ml of water, and washed with chloroform, then acidified with 30% sulfuric acid, and saturated with sodium chloride. Extraction with chloroform (3 × 50 ml) and concentration of the extracts gave a viscous oil which slowly solidified (5.3 g, 58%). Three recrystallizations from absolute ethanol gave a pure sample of IIe: mp 153–155° with gas evolution; λ_{max} 285 mμ; ν 1740, 1625 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.20; H, 6.14; N, 5.02. Found: C, 60.11; H, 6.18; N, 5.00.

1-Formyl-1,2,3,7,8,8a-hexahydro-5,6-dimethoxy-7-oxocyclopent[*ij*]isoquinoline (Ia). A.—A mixture of IId (5.00 g) in 50 g of polyphosphoric acid was stirred and heated at 100–110° for 80 min. The red-brown solution was cooled, decomposed with ice, and extracted with chloroform (4 × 50 ml). The extracts were dried over sodium sulfate, filtered through charcoal, and concentrated at reduced pressure. The residue was dissolved in 50 ml of benzene and stirred for 10 min with 3 g of alumina, then filtered, and concentrated. The residue was recrystallized from benzene–heptane to afford 0.20 g (4.7%) of a pale yellow solid, mp 138–144°, whose infrared spectrum was identical with that of the ketone prepared in part B.

B.—A solution of 100 mg of Ib in 20 ml of a 1:1 mixture of benzene and tetrahydrofuran was warmed while an ethereal solution of diazomethane was added over 15 min. Most of the solid material dissolved during the addition. The solvents were evaporated in a stream of nitrogen, and the light brown residue was recrystallized from benzene–heptane. The pale yellow plates of Ia (0.05 g), mp 145–146°, were recrystallized twice more to give the analytical sample: mp 146–147°; ν 1705, 1655 cm^{-1}; λ_{max} 236, 263, 346 mμ.

Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.79; N, 5.36. Found: C, 64.44; H, 5.93; N, 5.15.

1-Formyl-1,2,3,7,8,8a-hexahydro-5-methoxy-6-hydroxy-7-oxocyclopent[*ij*]isoquinoline (Ib).—A mixture of 1.00 g of IId and 10 g of polyphosphoric acid was heated at 140–150° for 30 min. The red-brown solution was poured over ice and extracted with chloroform. The orange extracts were dried over sodium sulfate, filtered through charcoal, and concentrated, yielding an oil which readily crystallized. The solid was washed with a few milliliters of benzene, leaving 170 mg (21%) of light brown ketone. Recrystallization from benzene–heptane gave the analytical sample: mp 203–205° dec; λ_{max} 265, 344 mμ; ν 1722, 1651 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.08; H, 5.43; N, 5.50.

Heating the acid IIc in polyphosphoric acid at 90–100° for 16 hr and working up as described gave a 2% yield of Ib.

On the Decomposition of Hindered Quinone Methides

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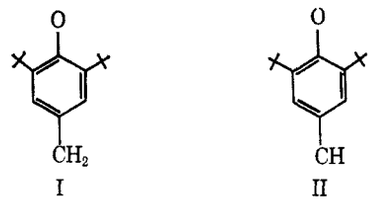
The esr spectrum of a 3,5-di-*t*-butyl-*p*-quinone methide has previously been interpreted by Coppinger, *et al.*,[1,2] to consist of equal parts of two free-radical species One is a triplet of triplets with approximate splitting constants of 9 and 2 gauss. These are said to represent the partial structures I and II. Our interest

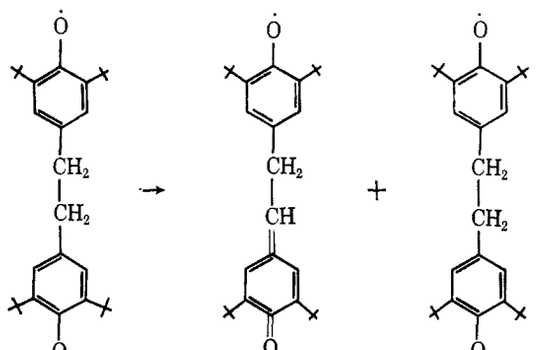


I II

in the reaction mechanisms of polymerization inhibitors[3–6] and the revival[7] of an earlier proposal[8] that the 2,6-di-*t*-butyl-4-methyl phenoxyl radical rearranged to form the 3,5-di-*t*-butyl-4-hydroxybenzyl radical has prompted a repetition of the above experiment.

The esr spectra obtained from varied concentrations of quinone methide indicate that the interpretation leading to radical II was an error which was probably due to low signal/noise ratio.

For the 0.25 *M* solution of 3,5-di-*t*-butyl-*p*-quinone methide, Figure 1 shows only a triplet of triplets with splitting constants of 7.67 and 1.67 gauss. From the experimental splittings in several phenoxy radicals,[9] it is reasonable to assign this spectrum, "A," to structure I in agreement with Coppinger. However, it is interesting that partial structure I can include such forms as the ones that are shown below (III–V).



III IV V

These should give nearly identical spectra since the π systems in the biradical III may be treated as separate entities.[9] Of course, esr cannot differentiate between any of these, but the presence of III is strongly inferred from a series of experiments by Neureiter.[10] Hydrogen abstraction from IV and/or III by V and/or III could lead to the final products, VI, 3,3′,5,5′-tetra-*t*-butylstilbene-4,4′-quinone, and VII, 1,2-bis(3,5-di-*t*-butyl-4-hydroxyphenyl)ethane. This step is suggested from experiments by Brodskii, *et al.*,[7] who found that

(1) G. M. Coppinger, *J. Am. Chem. Soc.*, **86**, 4385 (1964).
(2) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1201 (1963).
(3) R. H. Hoskins and B. R. Loy, *J. Chem. Phys.*, **28**, 2461 (1955).
(4) R. H. Hoskins, *ibid.*, **25**, 788 (1956).
(5) R. H. Hoskins, *ibid.*, **23**, 1975 (1955).
(6) R. H. Hoskins and B. R. Loy, unpublished Dow Chemical report, PRL No. 54126-3.
(7) A. I. Brodskii, V. D. Pokhodenko, and L. N. Ganyuk, *Roczniki Chemii*, **38**, 105 (1964).
(8) C. D. Cook, N. G. Nash, and H. R. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783 (1955).
(9) See, for example, "Free Radicals," D. J. E. Ingram, Ed., Academic Press Inc., New York, N. Y., 1958, p 230.
(10) N. P. Neureiter, *J. Org. Chem.*, **28**, 3486 (1963).

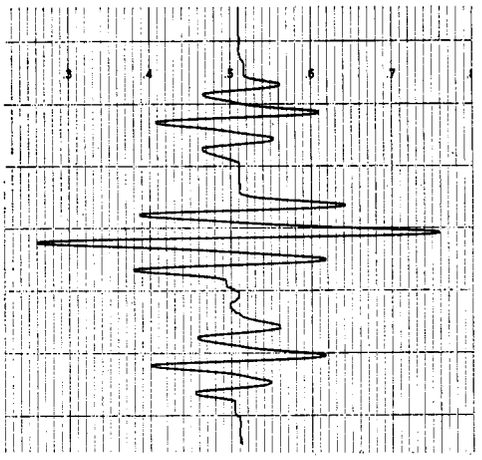


Figure 1.—Solution (0.25 M) of 3,5-di-t-butyl-p-quinone methide in carbon disulfide containing 3×10^{-5} M radicals represented by structure I. Splitting constants are 1.67 and 7.67 gauss.

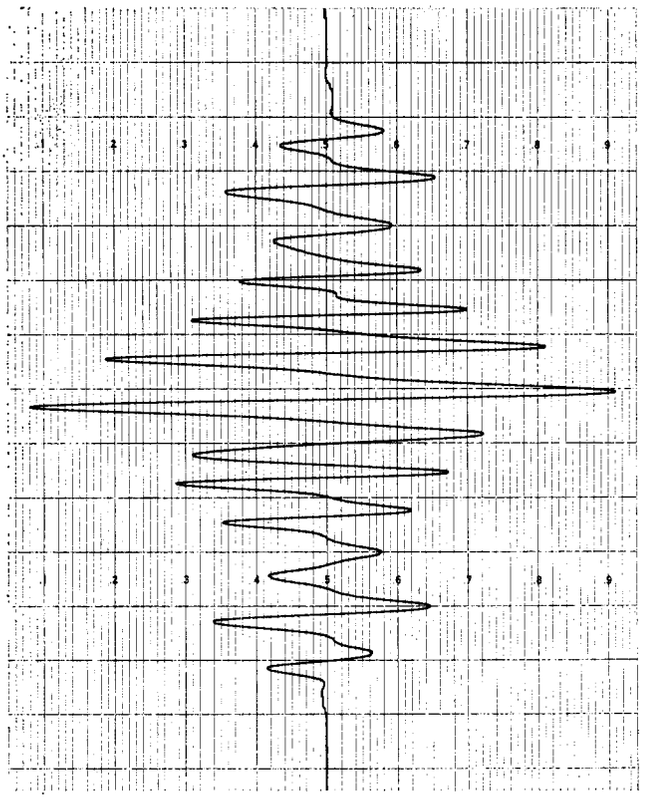
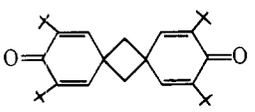


Figure 2.—Solution (0.10 M) of 3,5-di-t-butyl-p-quinone methide in carbon disulfide. Approximately 10^{-5} M in free radicals. Contains I plus galvinoxyl radical.

the phenolic-OD group in the parent 2,6-di-t-butyl-4-methyl phenol was replaced by OH in the oxidation product VII.

The experiments of Chandross and Kreilick[11] indicate that III would probably be in equilibrium with the internally dimerized structure that is shown below.



From a 0.1 M solution of the quinone methide, the spectrum shown in Figure 2 was found. This spectrum

(11) E. A. Chandross and R. Kreilick, *J. Am. Chem. Soc.*, **85**, 2530 (1963).

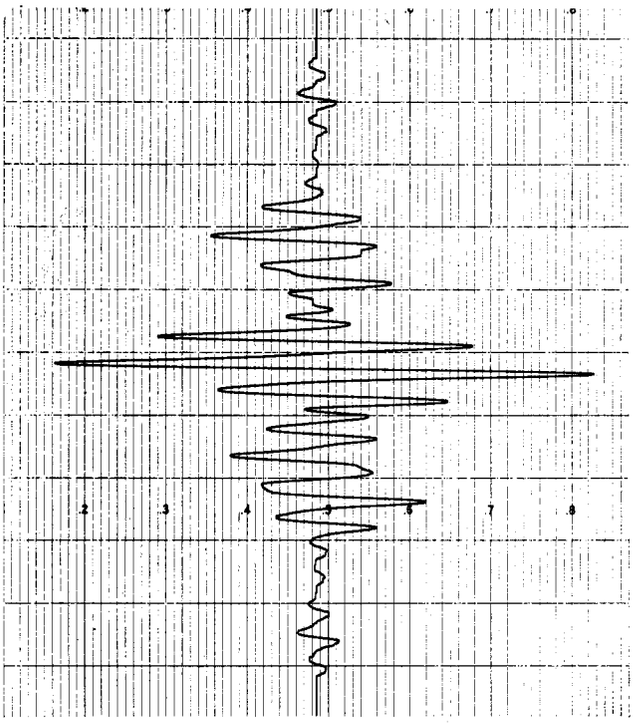


Figure 3.—All of the free radicals normally encountered in the (HgO in CS_2) oxidation of the parent phenol are present in this 0.05 M CS_2 solution of the quinone methide.

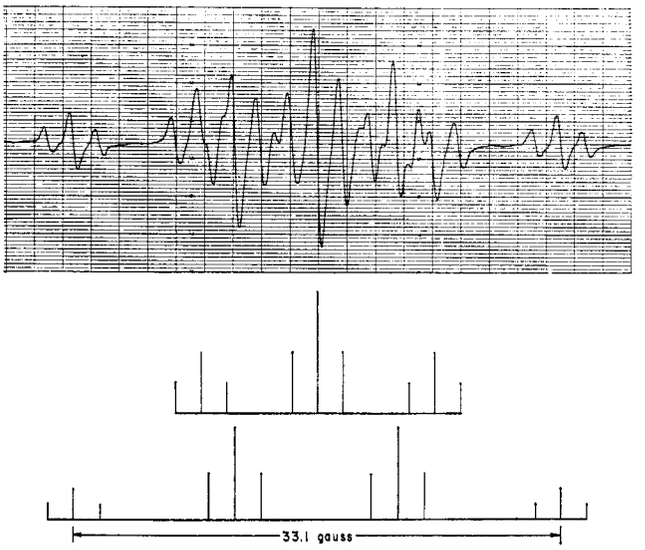


Figure 4.—Esr of reaction mixture during the (HgO–CS_2) oxidation of 2,6-di-t-butyl-4-methyl phenol shows primarily the 2,6-di-t-butyl-4-methyl phenoxyl radical and the radical in Figure 1.

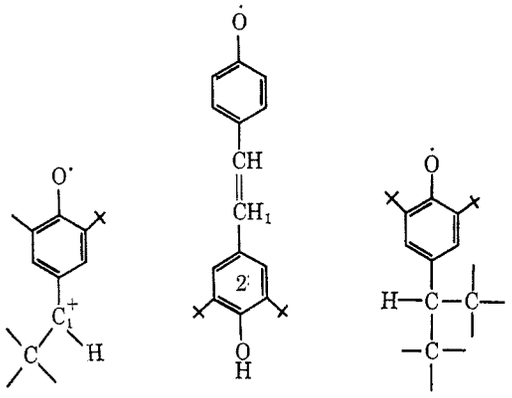
was also simulated by a computer program for summing gaussian lines which plotted the spectrum "A" plus another spectrum called "B," which is a pair of quintets with relative intensities of 1:4:6:4:1, splitting constants of 5.66 and 1.34 gauss and a line width of 0.4 gauss. The relative concentration of A/B is 1.7/1. "B" has been previously identified by Becconsall, *et al.*, to be the galvinoxyl radical,[12] which is relatively stable in this reaction media and may be ignored as an active intermediate.

Figure 3 shows the esr spectrum of a 0.05 M solution of the quinone methide. One recognizes that the pair

(12) J. K. Becconsall, S. Clough, and G. Scott, *Trans. Faraday Soc.*, **56**, 461 (1960).

of triplets, located at the extrema of the spectrum and which are 33.6 gauss apart, belong to the 2,6-di-*t*-butyl-4-methyl phenoxyl radical.[12] This is a quartet of triplets with splittings of 11.2 and 1.67 gauss and a line width of 0.53 gauss and is referred to as spectrum "C." Thus, Figure 3 is comparable to a computer simulated spectrum with relative concentrations A/B/C of 3.5/1.1/1. Figure 3 leaves no doubt that the phenoxyl radical is present even though its presence is difficult to explain except perhaps by the principle of microscopic reversibility. If one examines the spectrum shown in ref 1 it is apparent that, because of the poor signal–noise ratio, the "pair" of triplets was probably the two center triplets belonging to the phenoxyl radical.

Therefore, it is unlikely that II is a radical intermediate in the decomposition of the quinone methide. Further difficulties arise when one inquires about the nature of II. Possibly more complete structures include VIII–X.



VIII IX X

If VIII, then C_1 is sp^3 and only ring hydrogens will contribute to hyperfine splitting (hfs).[12,13] If IX, then H_1 and ring (2) hydrogens will contribute to hfs. X would produce the "observed" hfs but such a structure is unlikely.

In summary, one concludes that spectrum A is always noted in the decomposition of the quinone methide. B and C are present occasionally but these are identified as radicals which are not likely to be primary participants. A may be identified as the partial structure I[1] which in turn may represent the three structures III, IV and IV. Esr cannot distinguish between these but in view of known reactions,[7,10] it is likely that all three are present.

Perhaps, it is worthwhile to report that spectrum A has also been recorded during the oxidation of the parent phenol. Figure 4 was recorded after 131 min of reaction with mercuric oxide in carbon disulfide solution. The components are unambiguously interpreted to be equal parts of A and C.

Experimental Section

Preparation of 2,6-Di-*t*-butyl-4-bromomethylphenol (XI).—2,6-Di-*t*-butyl-4-methyl-4-bromo-2,5-cyclohexadienone, prepared after Coppinger and Campbell,[14] was heated in an evacuated, sealed Pyrex tube for 10 min at 100°. The nmr spectrum of the product dissolved in carbon disulfide showed the OH and CH_2Br peaks at τ 4.89 and 5.64 and indicated complete conversion to the benzyl bromide.

4-Methylene-2,6-(Di-*t*-butylcyclohexa-2,5-dienone (Quinone Methide).—After Filar and Winstein,[15] equivalent amounts of XI and triethylamine in carbon disulfide were mixed in the absence of air and filtered into a Varian sample tube. The nmr sample tube was welded to one end of a medium porosity Pyrex filter tube and a 4-mm glass tube fitted with a syringe cap was welded to the other end. The benzyl bromide solution was added through the syringe cap and frozen with liquid nitrogen. The triethylamine solution was similarly added. The argon atmosphere, which was previously added, was evacuated with a vacuum pump and the 4-mm glass tube was flame sealed. The contents were allowed to melt, shaken for 1 min at approximately −10°, and filtered by cooling the nmr tube in a Dry Ice bath. Finally the contents were frozen in liquid nitrogen while the nmr tube was flame sealed. The nmr spectrum was similar to that reported in ref 10 and indicated quantitative conversion to the quinone methide. In the case of the more concentrated solution (0.25 *M*), the radical (Figure 1) appeared to be in a steady-state concentration for about 3 hr and finally tailed off to a negligible concentration after 4 hr.

Oxidation of 2,6-Di-*t*-butyl-4-methylphenol (XII).—The mixture (0.0060 g of XII, 0.0250 g of mercuric oxide, and 0.18 ml of carbon disulfide) was sealed in a 4-mm Pyrex tube and examined in the esr spectrometer at 102° over a period of 24 hr. A similar mixture was prepared for nmr mesurements using the filtreing device described above. After 24 hr at 100° the hot mixture was filtered into the nmr tube. There was no precipitate formed after cooling to room temperature. The nmr spectrum of the filtrate showed the filtrate to be two parts VI and one part VII.

Instrumental.—The nmr[16] and esr[17] have been previously described.

Acknowledgments.—The author wishes to thank Dr. E. B. Baker for the use of the nmr spectrometer as well as Professor Earl Huyser and Dr. Corwin Bredeweg for helpful discussions. He also wishes to thank the reviewer for calling the work of Chandross and Kreilick[11] to his attention.

(13) E. J. Burrell, Jr., *J. Am. Chem. Soc.*, **83**, 574 (1961).
(14) G. M. Coppinger and T. D. Campbell, *ibid.*, **75**, 734 (1953).
(15) L. J. Filar and S. Winstein, *Tetrahedron Letters*, **No. 25**, 9 (1960).
(16) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **28**, 313 (1957).
(17) B. R. Loy and C. R. Noddings, *J. Catalysis*, **3**, 1 (1964), and references cited therein.

A New Preparation of 4-(*p*-Tolyl)-1,2-dithiole-3-arylimines

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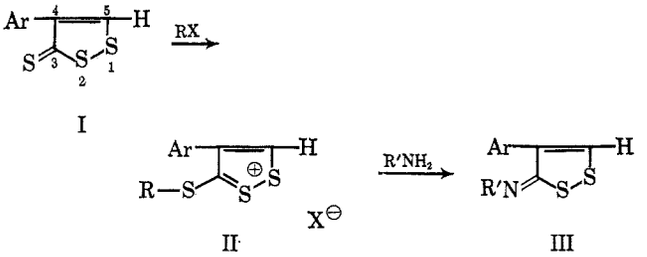
Trithionium salts (II), formed by the reaction of alkyl halides with 1,2-dithiole-3-thiones (I), react with amines to yield the 3-imines (III) and a mercaptan.[2a]



I II III

(1) Arapahoe Chemicals Inc., Boulder, Colo.
(2) (a) A. Luttringhaus and U. Schmidt, *Chem.-Ztg.*, **77**, 135 (1953); see *Chem. Abstr.*, **47**, 4836a (1953); (b) W. R. Diveley, K. Brack, and A. D. Lohr, *J. Agr. Food Chem.*, **12**, 251 (1964).