of the product prepared by methods A, B, and C were identical. Mixture melting points also established the identity of the products.

3,5'-Xanthosine Cyclonucleoside (IX).—2',3'-*O*-Isopropylidene-3,5'-xanthosine cyclonucleoside (VII, 4 g.) was stirred overnight in 30 ml. of 1 *N* hydrochloric acid. The solution was neutralized to pH 7 with ammonium hydroxide and then evaporated to dryness *in vacuo*. The solid residue was dissolved in a minimum amount of hot water, and the solution was allowed to cool overnight in the refrigerator. The solid that precipitated was filtered to yield 1.8 g. A small sample was recrystallized from a little water to give a product, m.p. 222–224°; ultraviolet data, $\lambda_{\max}^{\text{pH }1}$ 265 and 240 mμ (ε 8000 and 6500), $\lambda_{\max}^{\text{pH }11}$ 267 mμ (ε 9100).

Anal. Calcd. for $C_{10}H_{10}N_4O_5$: C, 45.1; H, 3.8; N, 21.1. Found: C, 44.7; H, 3.4; N, 21.4.

3-5'(5'-Deoxy-D-ribofuranosyl)xanthosine (X).—2',3'-*O*-Isopropylidene-3,5'-xanthosine cyclonucleoside (VII, 2 g.) was dissolved in 50 ml. of 1 *N* hydrochloric acid. The solution was heated for 1 hr. on the steam bath, cooled, treated with charcoal, filtered, and neutralized to pH 7 with ammonium hydroxide. The resulting solution was evaporated to dryness *in vacuo*, and the residue was dissolved in a minimum amount of hot water and allowed to cool overnight in the refrigerator. The precipitate was filtered and recrystallized from water to give a product (0.6 g.), m.p. 179–182° dec.; ultraviolet data, $\lambda_{\max}^{\text{pH }1}$ 269 mμ (ε 10,200), $\lambda_{\max}^{\text{pH }11}$ 274 mμ (ε 11,700).

Anal. Calcd. for $C_{10}H_{12}N_4O_6$: C, 42.3; H, 4.2; N, 19.7. Found: C, 41.9; H, 4.5; N, 19.4.

3-5'(5'-Deoxy-D-ribofuranosyl)adenine (XIII).—2',3'-*O*-Isopropylidene-3,5'-adenosine cyclonucleoside *p*-tolylsulfonate[3] (3 g.) was added to 30 ml. of 1 *N* hydrochloric acid. The solution was heated on the steam bath for 40 min., cooled, treated with charcoal, filtered, neutralized to pH 7 with ammonium hydroxide, and evaporated to dryness *in vacuo*. The residue was dissolved in a small amount of hot water, and the solution was cooled overnight in the refrigerator. The resulting precipitate was filtered and recrystallized from water to yield 0.9 g. of product, m.p. >180° dec.; ultraviolet data, $\lambda_{\max}^{\text{pH }1}$ 274 mμ (ε 18,000), $\lambda_{\max}^{\text{pH }11}$ 274 mμ (ε 12,600).

Anal. Calcd. for $C_{10}H_{13}N_5O_4\cdot H_2O$: C, 42.1; H, 5.3; N, 24.6; H_2O, 6.3. Found: C, 41.8; H, 5.5; N, 24.4; H_2O, 6.9.

2',3'-*O*-Isopropylidene-3,5'-inosine Cyclonucleoside *p*-Tolylsulfonate.—2',3'-*O*-Isopropylidene-5'-*O*-(*p*-tolylsulfonyl)inosine[11] (5 g.) was heated, with continuous stirring, in 60 ml. of refluxing dioxane. Solution was complete after 10–15 min., and after 2 hr., a white precipitate began to form. Heating was continued for another 2 hr., and then the solution was cooled overnight in the refrigerator. The precipitate was filtered, washed with a little ethanol, and recrystallized from ethanol to yield 4.1 g. of product, m.p. 188–191° dec. The infrared spectrum exhibited no covalent *p*-tolylsulfonate band at 8.5 μ but showed an ionic *p*-tolylsulfonate band at 9.8 μ; ultraviolet data, $\lambda_{\max}^{\text{pH }1}$ 255 mμ (ε 10,600), $\lambda_{\max}^{\text{pH }11}$ 257 mμ (ε 9700).

Anal. Calcd. for $C_{20}H_{22}N_4O_7S$: C, 51.9; H, 4.8; N, 12.1. Found: C, 52.0; H, 4.9; N, 11.9.

2',3'-*O*-Isopropylidene-3,5'-inosine Cyclonucleoside (XII).—2',3'-*O*-Isopropylidene-3,5'-inosine cyclonucleoside *p*-tolylsulfonate (5 g.) was dissolved in 30 ml. of water, and the pH of the solution was adjusted to 7 with 14% aqueous ammonia. The solution was stirred for 6 hr., during which time a precipitate gradually formed. The mixture was then cooled and filtered and the product recrystallized from ethanol to yield 1.9 g., m.p. 266–269° dec. The infrared spectrum showed no ionic *p*-tolylsulfonate band at 9.8 μ; ultraviolet data, $\lambda_{\max}^{\text{pH }11}$ 256 mμ (ε 8600).

Anal. Calcd. for $C_{13}H_{14}N_4O_4\cdot H_2O$: C, 50.6; H, 5.2; N, 18.2. Found: C, 50.6; H, 5.2; N, 18.2.

New Reaction of a Quinone Methide

NORMAN P. NEUREITER

Humble Oil and Refining Company, Research and Development, Baytown, Texas

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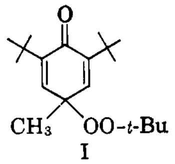
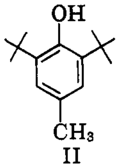
From the reaction of the quinone methide III with 2,6-di-*t*-butylphenol a 17% yield of compound VI has been isolated. A possible mechanism for its formation is discussed, as well as the implications of such a mechanism for inhibition of oxidation by 2,6-di-*t*-butyl-4-methylphenol.

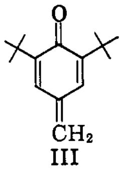
Considerable effort has been devoted in our studies of the mechanism of antioxidant action[1] to the chemistry of the 4-peroxydienone intermediate I which is formed from the reaction of 2,6-di-*t*-butyl-4-methylphenol (II) with *t*-butylperoxy radicals.[2] The formation of certain products during reduction or thermal decomposition of I suggested the intermediacy of the quinone methide III.[3] Accordingly, a study of the reactions of III was undertaken. While little evidence was acquired for the postulated appearance of III during reactions of I, the work was redeemed by an intriguing peripheral dividend. This paper describes a previously unreported reaction of the quinone methide III.



I

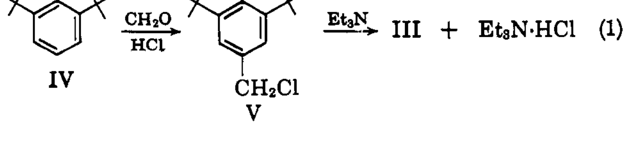


II



III

For the preparation of III, 2,6-di-*t*-butylphenol (IV) was chloromethylated and the reaction product in petroleum ether (b.p. 30–60°) was treated with triethylamine[4] (eq. 1). When the clear yellow filtrate after removal of the solid amine hydrochloride was let stand, the color steadily deepened. After several days the dark red solution had deposited a small quantity of large colorless crystals, which after recrystallization from chloroform and methanol melted at 264–265° with some decomposition. Exposure to light and air resulted in a gradual yellowing of the solid.



Elemental analysis, molecular weight determination,

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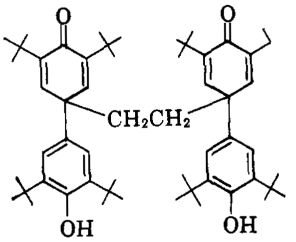
[1] N. P. Neureiter and D. E. Bown, *Ind. Eng. Chem. Prod. Res. Develop. Quart.*, **1**, 236 (1962).

[2] Many peroxides of this type are known. See T. W. Campbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **74**, 1469 (1952); C. D. Cook, R. C. Woodworth, and P. Fianu, *ibid.*, **78**, 4159 (1956); A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 638 (1953); C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 (1955).

[3] Unpublished work by N. P. N.

[4] This procedure was used by L. J. Filar and S. Winstein, *Tetrahedron Letters*, No. **25**, 9 (1960).

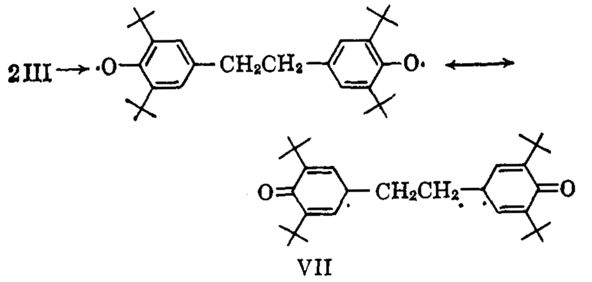
and the infrared, ultraviolet, and n.m.r. spectral properties as described in the Experimental section were deemed consistent only with the tetranuclear structure VI, 4,4′-ethylenebis[2,6-di-*t*-butyl-4-(3,5-di-*t*-butyl-4-hydroxyphenyl)cyclohexa-2,5-dienone].



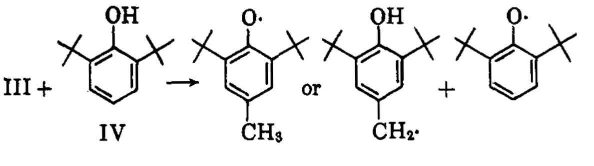
VI

It was later found that the solution of quinone methide had been contaminated with some 40% of nonchloromethylated 2,6-di-*t*-butylphenol (IV). With the aid of gas chromatography or n.m.r. it was readily demonstrated that VI was formed by the reaction of IV with the quinone methide. In the absence of IV no VI was formed.

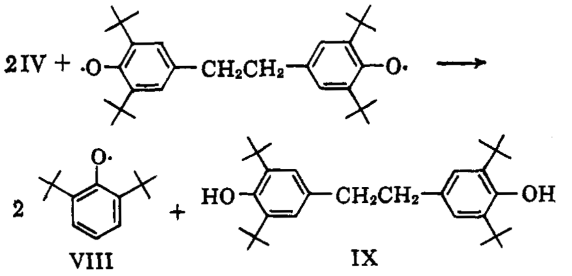
There are two simple competing reactions in which quinone methide could be consumed. One is dimerization (eq. 2). The other is an oxidation–reduction reaction between the quinone methide and the phenol IV (eq. 3). It is our feeling that reaction 2 provides more reasonable access to the product VI than reaction 3, although it is difficult to exclude the latter explicitly. Presumably the phenol IV intercedes after reaction 2 *via* a reduction mechanism (eq. 4).



(2)

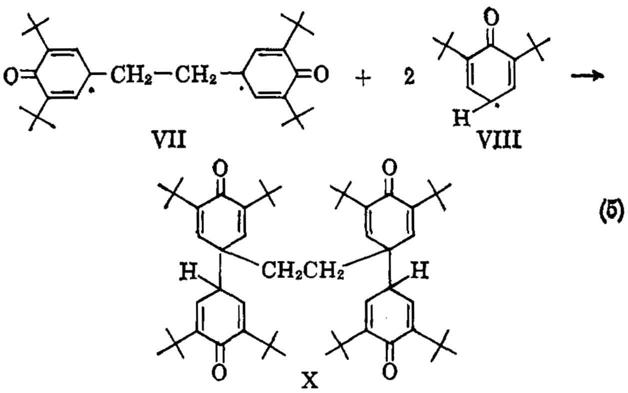


(3)



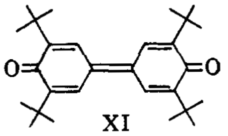
(4)

Subsequently VIII couples with more of diradical VII (eq. 5). After simple tautomeric shift of two hydrogens X is identical with the observed product VI. The following experimental facts are offered in support of our mechanistic contentions.



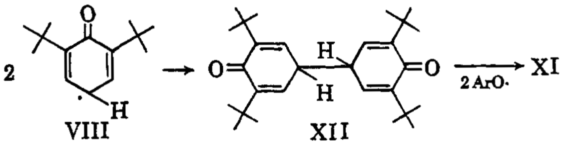
(5)

The yield of VI was a function of the ratio of the quinone methide III to the phenol IV. With a twofold molar excess of IV over III, no product VI was obtained. An n.m.r. spectrum indicated that the reaction mixture contained principally the bibenzyl IX along with unchanged IV, and apparently some of the diphenoquinone XI (based on the hydrogen resonance peak at 2.31 τ).[5] It seems apparent that the 2,6-di-*t*-butylphenol is capable of donating hydrogen atoms to the diradical



XI

VII formed by dimerization of the quinone methide. The fate of the 2,6-di-*t*-butylphenoxyl (VIII) in the absence of a sufficiency of a material with which it can couple is dimerization to XII followed by oxidation of this convenient hydrogen donor to XI by other aroxyl radicals in the solution (eq. 6).



(6)

When 0.5 mole of IV was treated with 1 mole of quinone methide at room temperature the yield of VI was 5%. At −15° under nitrogen the same IV to III ratio gave a 17% yield of VI—the highest value obtained. The stoichiometry of eq. 2, 4, and 5 taken together requires this 1:2 molar ratio of IV to III for a maximum yield of VI.

Evaporation of a solution of the pure quinone methide without any IV left principally the stilbenediquinone XIII and the bibenzyl IX.[6] Any other products present were not identified. The absence of a 10.45-μ band in the infrared spectrum of the product indicated that there was litte, if any, of XIV which would be the product of intramolecular disproportionation of VII. In high concentrations the quinone methide apparently readily dimerizes to VII, which in the absence of other reagents undergoes an intermolecular disproportionation to IX and XIII.

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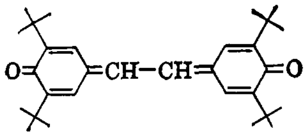
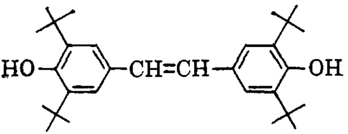
(5) This position is identical with the value determined for the quinone ring hydrogens in XI by S. Brownstein and K. U. Ingold, *J. Am. Chem. Soc.*, **84**, 2258 (1962).

(6) The stilbenediquinone XIII was the only product from concentration of a solution of the quinone methide reported by Filar and Winstein, *Tetrahedron Letters*, No. **25**, 9 (1960).



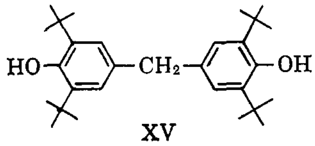
XIII



XIV

When the reaction was carried out at ~45° (gentle reflux) with slow addition of the phenol IV, no VI was obtained although the solution rapidly developed the characteristic red color. Higher temperatures would favor hydrogen abstraction reactions by the aroxyls over simple coupling.

The best piece of evidence against reaction 3 is the failure to find in the n.m.r. spectra of the reaction products resonance peaks corresponding to coupling products such as XV, which would be formed from the reaction of benzyl radicals with aroxyls such as VIII. If the phenol were capable of transferring hydrogen to the quinone methide to give a benzyl radical, XV could be expected to be present in significant quantities.

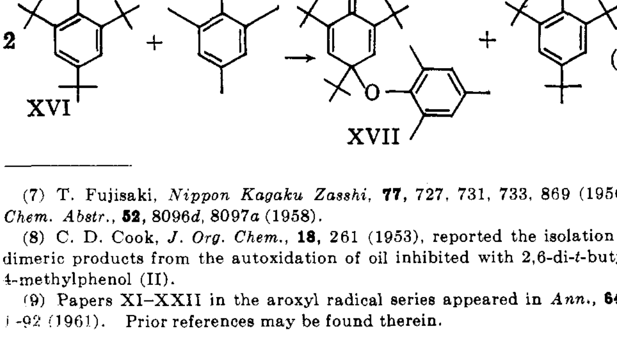


XV

Finally, the reaction mixture after separation of VI contained principally the bibenzyl IX, some of the stilbenediquinone XIII, smaller amounts of the diphenoquinone XI (from n.m.r.), and some unidentified materials. The presence of a considerable amount of IX is consistent with the reaction path shown in eq. 2 and 4.

Fujisaki[7] has presented evidence that the principal products from self-condensation reactions of the quinone methide are the bibenzyl derivative IX, the stilbenediquinone XIII, and under different conditions the dihydroxystilbene XIV. He concluded that the quinone methide was intermediate in the formation of dimeric products during the oxidation of II.[8] He pointed out that the reactions of the quinone methide varied markedly with the temperature.

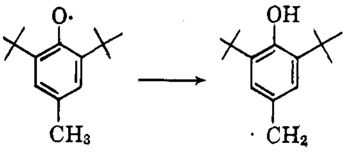
The dehydrogenation of a phenol by an aroxyl radical is not new. The impressive mass of experimental data which has been accumulated by E. Müller and co-workers[9] adequately attests to the strong and broadly applicable dehydrogenating activity of certain aroxyls, in particular 2,4,6-tri-*t*-butylphenoxyl (XVI). The products of these reactions have generally been construed to be quinol ethers as in the reaction of XVI and 2,4,6-trimethylphenol to give XVII (eq. 7).



(7)

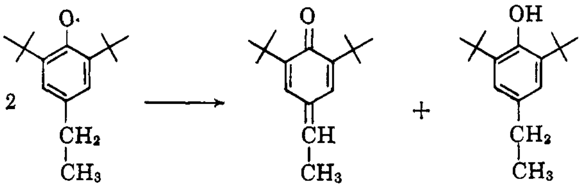
We see in this work very convincing evidence that in concentrated solutions the quinone methide is unstable with respect to its diradical dimer VII which then disports among a variety of subsequent reaction paths determined by the chemical environment. In the presence of appropriate radicals such as VIII this diradical may be trapped with an efficiency which is surprising in view of the large number of competing reactions.

One may be able to extrapolate from these results to the formation of dimeric products during autoxidation inhibited by II. C. D. Cook, *et al.*, reported the rearrangement of 2,6 di-*t*-butyl-4-methylphenoxyl (XIX) to the 3,5-di-*t*-butyl-4-hydroxybenzyl radical XX (eq. 8) which then underwent dimerization.[10]



(8)

Since it is known that the following disproportionation (eq. 9) takes place very rapidly,[11a] and since the same reaction path is probably available to the 2,6-di-*t*-butyl-4-methylphenoxy radical (XIX) which is even more reactive,[11a] it may not be necessary to invoke an aroxyl to benzyl radical rearrangement to account for dimeric materials. This is particularly pertinent if VII is capable of dehydrogenating II as it was with IV.



(9)

One preliminary experiment with 0.5 mole of II (in place of IV) and 1 mole of quinone methide gave a mixture of 75–80% of the bibenzyl IX, and only about 20% of the stilbenediquinone. There was, in addition to some unchanged II, a small amount of uncharacterized material, the infrared spectrum of which showed strong absorption resembling cyclohexadienone. While not conclusive, the experiment suggested a continuous cycle.

$$2\ \text{III} \longrightarrow \text{VII} \tag{10}$$

$$\text{VII} + 2\ \text{II} \longrightarrow \text{IX} + 2\ \text{XIX} \tag{11}$$

$$2\ \text{XIX} \longrightarrow \text{III} + \text{II} \tag{12}$$

The net process is III + II → IX.

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[7] T. Fujisaki, *Nippon Kagaku Zasshi*, **77**, 727, 731, 733, 869 (1956); *Chem. Abstr.*, **52**, 8096*d*, 8097*a* (1958).

[8] C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953), reported the isolation of dimeric products from the autoxidation of oil inhibited with 2,6-di-*t*-butyl-4-methylphenol (II).

[9] Papers XI–XXII in the aroxyl radical series appeared in *Ann.*, **645**, 1-92 (1961). Prior references may be found therein.

[10] C. D. Cook, N. G. Nash, and M. R. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783 (1955).

[11] (a) C. D. Cook and B. E. Norcross, *ibid.*, **81**, 1176 (1959); E. Müller, R. Mayer, U. Heilmann, and K. Scheffler, *Ann.*, **645**, 66 (1961). (b) NOTE ADDED IN PROOF.—Since this work was completed, R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1201 (1963), have reaffirmed their early established competence in this field with convincing evidence for the disproportionation reaction of the 2,6-di-*t*-butyl-4-methylphenoxy radical to the quinone methide and the phenol. They further showed that the quinone methide dimerizes through a radical species which then disproportionates into the stilbenediquinone and the bibenzyl derivative discussed above. The previously postulated rearrangement of the phenoxy to the benzyl radical is further jeopardized by their experiments. Their data are fully consistent with the conclusions offered in the present work.

The competition between abstraction–disproportionation reactions leading to stilbenediquinone and reduction reactions leading to the bibenzyl must depend closely on conditions of temperature and concentration of reagents. With proper conditions it might be possible to form the bibenzyl IX to the nearly complete exclusion of the stilbenediquinone without going through a benzyl radical intermediate.[11b]

Experimental[12]

Preparation of 2,6-Di-*t*-butyl-4-chloromethylphenol.—A vigorously stirred mixture of 2,6-di-*t*-butylphenol (Ethyl Corp. AN-1, 52.8 g., 0.256 mole), formaldehyde (250 ml. of 37% solution), concentrated hydrochloric acid (500 ml.), and *n*-heptane (200 ml.) in a 2-l. creased flask was gently refluxed under nitrogen for 6 to 14 hr. The organic layer was diluted with 100 ml. of petroleum ether and shaken 5 to 8 times with water (until wash liquid was neutral), dried with sodium sulfate or Drierite, and the total product diluted to 500 ml. with petroleum ether in a volumetric flask. The solutions were always yellow and when the long reflux times were used for chloromethylation they were light orange. Concentration of an aliquot gave a yield of 98–100%. The n.m.r. spectrum of the concentrate indicated it to be essentially pure (at least 95%) despite the yellow color. Aliquots (100 ml., 0.051 mole) of the solution were used for the quinone methide syntheses.

4-Methylene-2,6-di-*t*-butylcyclohexa-2,5-dienone (Quinone Methide).—The method was adapted from Filar and Winstein.[4] A solution of triethylamine (5.15 g., 0.051 mole) in petroleum ether (25 ml.) was added with swirling to a solution of the chloromethylated phenol (13.0 g., 0.051 mole) in petroleum ether (~175 ml.) while crude cooling was carried out in a −15° bath and nitrogen was blown into the flask. The mixture was let stand for 2–3 min. with occasional swirling and, again with crude nitrogen blanketing, was filtered through a coarse fritted disk funnel under vacuum. The precipitate was washed two or three times with petroleum ether (total of ~150 ml.). In a typical experiment the white precipitate after drying *in vacuo* weighed 7.02 g. (100% calculated as triethylamine hydrochloride), though the orange spots on the solid indicated that not all of the quinone methide material had been washed out. When the total filtrate was concentrated *in vacuo*, the dark red solid residue weighed 10.65 g. corresponding to a 96% yield of the quinone methide. The solution of the quinone methide very rapidly darkened in color. It was necessary to use it immediately after preparation.

The quinone methide also could be prepared in carbon tetrachloride by adding triethylamine directly to the carbon tetrachloride solution of the 2,6-di-*t*-butyl-4-chloromethylphenol and washing the precipitate with carbon tetrachloride. The n.m.r. spectrum of the resulting yellow solution had three sharp peaks corresponding to the expected three types of hydrogens: at 3.18 (two hydrogens on the quinone nucleus), at 4.38 (two methylene hydrogens), and 8.73 τ (18 hydrogens in the *t*-butyl groups). Even after a few minutes a small per cent of *t*-butyl groups on dimeric products was apparent from the peaks appearing between 8.6 and 8.7 τ. Changes in the spectrum were observed over an 18-day period. In addition to the three sharp peaks in the *t*-butyl region attributable to the bibenzyl IX (8.60) and stilbenediquinone XIII structures (8.64 and 8.67 τ) there were several smaller peaks not accounted for satisfactorily.

Reaction of Quinone Methide with 2,6-Di-*t*-butylphenol for the Synthesis of VI.—The product VI was originally found by accident when a petroleum ether solution of the quinone methide produced from the chloromethylphenol contaminated with 2,6-di-*t*-butylphenol was let stand for several days at room temperature. The best procedure found for preparation of VI was the following.

The quinone methide (0.051 mole) in petroleum ether solution (at ~0°) was filtered with crude nitrogen blanketing as previously described into a filter flask equipped with a magnetic stirrer and containing a solution of 2,6-di-*t*-butylphenol (0.025 mole) cooled to −20° in a cooling bath. The volume of the solution, which after washing was 350–400 ml., was reduced to 175–200 ml. *in vacuo* on a rotating evaporator. The resulting solution was blown with nitrogen for a few minutes and placed in a refrigerator at −15 to −20° for three days. After 20 hr., precipitation of large colorless crystals of VI had begun. On the second day a precipitate of fine reddish brown powder (A) began to separate, along with some clumps of white solid (B). When the solution was filtered, the combined precipitates weighed 2.4 g. The product VI was purified by pulverizing the total product, boiling with methanol, and filtering while warm. Cooling of the methanol solution gave a precipitate of yellow solid (should have been colorless) of B, m.p. 170–171°, which on the basis of its infrared spectrum was concluded to be the ethylenebisphenol IX. A was concluded to be the stilbenediquinone XIII. Final purification of VI could be achieved by dissolution in chloroform and precipitation with either methanol or carbon tetrachloride. The yield of once recrystallized material was 1.54 g. (in two crops). A small additional yield (0.21 g.) was obtained by boiling the concentrated reaction mixture with methanol, filtering while hot, and recrystallizing the residue from chloroform–methanol. The total yield of VI was 17% based on the quinone methide.

Experiments were carried out at different molar ratios of quinone methide to phenol. For 1:2, the yield of recovered VI was 0.0% (25° for 5 days, followed by 0° for 15 days); for 1:1, the yield was 1.8% (14 days at 0°); at 1:0.75, the yield was 12% (5 days at −15°); at 1:0.5, the yield was 9% (3–4 days at 0°), and 17% (3 days at −15 to −20°). When a run was made at the reflux temperature of ~45° with slow addition of 0.5 mole of the 2,6-di-*t*-butylphenol over about 2 hr., the solution turned rapidly to a deep red and on cooling after 24 hr. of refluxing a fine precipitate of red solid was formed. After 10 days at room temperature the flask was put in the ice box at 0° for 2 weeks. Only the bibenzyl IX and dark red quinone XIII material were isolated. No VI was recovered. When the synthesis of VI was carried out in carbon tetrachloride at −15°, precipitation of the product appeared somewhat slower. After 17 days filtration and recrystallization gave an 8% yield of VI.

Characterization of VI.—The material could be recrystallized from chloroform–methanol to give a colorless solid, m.p. 164–265°. The sample turned yellow on heating in air and melted to an orange-red liquid. The cooled liquid remelted at 254–259° indicating that some decomposition had occurred. The color was characteristic of the red stilbenediquinone structure XIII. The infrared spectrum in carbon disulfide or in chloroform showed bands characteristic of a 1,2,3,5-substituted benzene ring between 740 and 820, *t*-butyl groups at 1365 and 1390, and a hindered OH group at 2700 cm.$^{-1}$. The strong doublet at 1630 and 1650 cm.$^{-1}$ was similar to the bands in the 4-substituted cyclohexadienone structure I. An ebulliscopic molecular weight determination in benzene gave a value of 830 indicating four six-carbon nuclei to be involved.

The n.m.r. spectrum[13] gave unequivocal support to the structure VI. In deuteriochloroform with a tetramethylsilane standard there were six peaks attributable to two aromatic hydrogens at 3.03, two quinoid ring hydrogens at 3.57, two hindered phenolic hydroxyls at 4.90, two ethylenic hydrogens on a carbon beta to both an aromatic ring, and a quinoid system at 8.10,[14] 18 hydrogens in *t*-butyl groups on an aromatic ring at 8.60, and 18 hydrogens in *t*-butyl groups on a quinoid ring at 8.69 τ, respectively.

The ultraviolet spectrum was run in ether, $\lambda_{\max}$ 235, ϵ 37,000; 277, ϵ 4500; 365 mμ, ϵ 47. These values were compared with those for 2,6-di-*t*-butyl-4-methyl-4-*t*-butylperoxycyclohexa-2,5-dienone (I), $\lambda_{\max}$ 234, ϵ 10,600; 373, ϵ 22.5; and with 2,6-di-*t*-butyl-4-methylphenol (II), $\lambda_{\max}$ 277, ϵ 2000; at 235 mμ, ϵ ~ 2000. Except for the necessity of assuming some enhancement of the 235-mμ band in VI which results in nonadditivity of the molar extinction coefficients for the individual chromophoric units, the ultraviolet spectrum is in excellent accord with the postulated structure.

Anal. Calcd. for $C_{58}H_{88}O_4$: C, 82.2; H, 10.2; O, 7.6. Found: C, 82.1; H, 10.3.

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[12] Melting points are uncorrected. Combustion analyses were by E. Bowers of the Humble Oil and Refining Co. Infrared spectra were run on a Perkin-Elmer Model 21 infrared spectrophotometer or on a Baird Associates instrument equipped with sodium chloride optics. Ultraviolet spectra were run on a Cary Model 14 recording spectrophotometer.

[13] Spectra were run on a Varian Associates A-60 n.m.r. spectrometer. Hydrogen resonance peak positions are average values of two runs 7 months apart. Accuracy of the values is considered to be ±0.5%.

[14] Using principles of the Humble shift charts and values in the expanded "Humble Catalog of N.M.R. Spectra" [See N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959)], a theoretical value of 8.1 τ was calculated for these hydrogens.

Acknowledgment.—Only the ability to utilize the considerable competence of a large number of people at Humble Research and Development has permitted the successful conclusion of this work. In particular the author's thanks are due L. Westerman and J. O. Brewer for the molecular weights, N. F. Chamberlain and T. Hines for the n.m.r. spectra, and S. H. Hastings, H. W. Kinsey, and T. Reid for the ultraviolet spectra. The author is grateful to the Humble Oil and Refining Company for permission to publish these results.

Reactions of (Chloromethyl)alkylsilanes and Quinoline[1]

RALPH J. FESSENDEN AND JOAN S. FESSENDEN

Department of Chemistry, San Jose State College, San Jose, California

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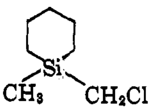
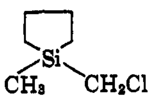
A reassignment of the structures of the (α-chloro)dimethylsilacyclopentanes has been made on the basis of n.m.r. spectra. Upon reflux with quinoline, (chloromethyl)alkylsilanes undergo cleavage of the chloromethyl group to yield chlorosilanes or, with water work-up, disiloxanes.

In a previous study,[2] we investigated the free-radical chlorination of dimethylsilacyclopentane and dimethylsilacyclohexane and assigned structures to the monochlorinated products. After completion of that work, it was brought to our attention that the n.m.r. spectrum of the compound designated 1-chloromethyl-1-methylsilacyclohexane (**1**) was not in agreement with our assigned structure.[3] Since the structure assigned to this compound was based upon analogy from the more extensively investigated 1-chloromethyl-1-methyl-silacyclopentane (**2**) and 1,1-dimethyl-2-chlorosilacyclopentane (**3**), we were prompted to investigate the n.m.r. spectra of the two isomers and to reinvestigate the chemistry leading to our original structure assignments.



1



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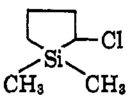
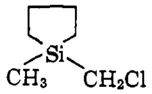
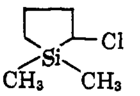


3

An assignment of structures to **2** and **3** can be made with the aid of the characteristic chemical shifts and splitting patterns of the chloroalkyl protons observed in the n.m.r. spectra. The n.m.r. spectra of some reference compounds along with the n.m.r. spectra of the (monochloroalkyl)dimethylsilacyclopentanes are summarized in Table I. The (chloromethyl)silanes show a sharp singlet in the region of interest while the (α-chloroethyl)silanes (examined to determine the chemical shift rather than the splitting pattern) exhibit a quartet. In the spectra of the (α-chloro)dimethylsilacyclopentanes, the isomer previously assigned structure **2**, b.p. 156–157°, showed a well defined triplet; the isomer previously assigned structure **3** exhibited a sharp singlet. It is apparent from this spectral data that the original structure assignments were reversed.

TABLE I

CHEMICAL SHIFTS AND SPLITTING PATTERNS OF SOME (CHLOROALKYL)SILANES[a]

Compound	Chemical shift of the chloroalkyl protons, p.p.m.	Splitting pattern
$(CH_3)_3SiCH_2Cl$	2.68	Singlet
$CH_3(C_2H_5)_2SiCH_2Cl$	2.68	Singlet
	2.75	Singlet
$C_2H_5(CH_3)_2SiCH(Cl)CH_3$	3.25	Quartet $J = 7$ c.p.s.
	3.30	Triplet $J = 5$ c.p.s.

[a] Ref. 9.

In our original work,[2] the key step in the structure proof was a quinoline dehydrohalogenation. It was reasoned that **3** would react to yield an olefin while **2** would not react. Indeed, when the reaction was carried out, one of the α-chloro isomers underwent reaction with quinoline while the other was recovered from the reaction mixture along with some olefinic material. In that it later became apparent that **2** reacts with quinoline at a faster rate than does **3**, it was of interest to determine the nature of this reaction.

It was observed that (chloromethyl)trimethylsilane (**4**) and (chloromethyl)diethylmethylsilane (**5**) both undergo cleavage of the chloromethyl group when heated under reflux with quinoline. With **4**, after a 3-day reflux with quinoline, trimethylchlorosilane was isolated in 70% yield. Shorter reflux periods resulted in substantially lower yields of the chlorosilane. With **5**, a 24-hr. reflux with quinoline and water work-up resulted in a 75% yield of the disiloxane (**6**).

$$\underset{\mathbf{4}}{(CH_3)_3SiCH_2Cl} \xrightarrow{\text{quinoline}} (CH_3)_3SiCl$$

$$\underset{\mathbf{5}}{CH_3(C_2H_5)_2SiCH_2Cl} \xrightarrow[\text{2. } H_2O]{\text{1. quinoline}} \underset{\mathbf{6}}{[CH_3(C_2H_5)_2Si]_2O}$$

Under the same conditions as used with **5**, (α-chloroethyl)dimethylethylsilane yielded only traces of vinyl(dimethyl)ethylsilane, while 70% of the starting (α-chloroethyl)silane was recovered.

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[2] R. J. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 2003 (1961).

[3] (a) We are grateful to S. Brownstein, National Research Council, Canada, for bringing to our attention the incompatibility of the n.m.r. spectrum of **3** and our previously assigned structure. (b) Although the (chloro)dimethylsilacyclohexane was not completely characterized, the position of the chloroalkyl proton multiplet (3.2 p.p.m.) in the n.m.r. spectrum indicates that the chlorine is attached to the 2-position rather than the 3-position of the ring. The multiplicity of this band is attributed to the conformations of the ring.