Synthesis and Reactions of 2,6-Dimethyl-7,7-dicyanoquinonemethide

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Received March 16, 1964

The preparation of 2,6-dimethyl-7,7-dicyanoquinonemethide by the reaction of 2,6-dimethylphenol with thionyl chloride followed by treatment with malononitrile is described. This quinonemethide was treated with phenols, anthrone, N,N-dimethylaniline, and malononitrile to yield 1,6-addition products.

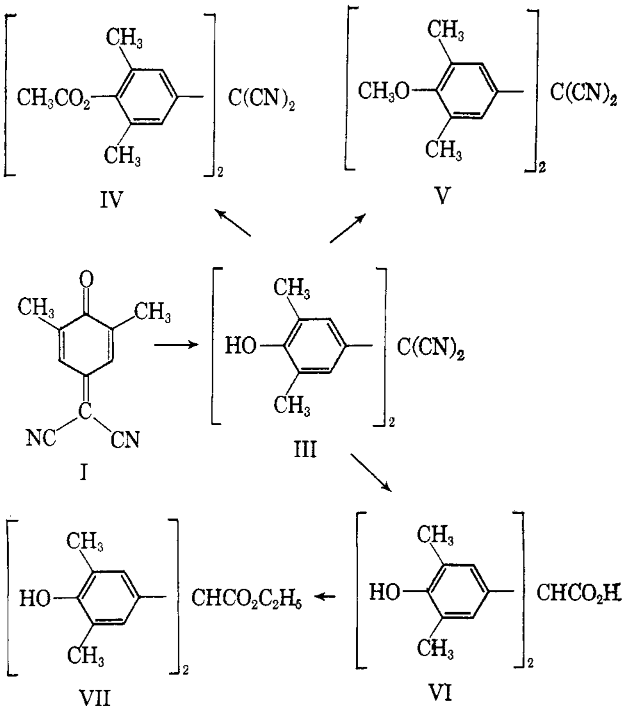
In this report the preparation and some reactions of 2,6-dimethyl-7,7-dicyanoquinonemethide (I) are described. Comparatively few compounds possessing the *p*-benzoquinonemethide structure have been reported[1] in the literature. Although 2,6-dialkylquinonemethides[1c,d] have been prepared in solution either by the dehydrohalogenation of the corresponding 4-halomethylphenols or by the oxidation of the 4-alkylphenols, the extreme instability of these compounds did not permit their isolation and characterization. The attempted isolation of these compounds lacking substituents on the methylene carbon generally resulted in dimerization. On the other hand the oxidation of 2,6-di-*t*-butyl-4-(2-propyl)phenol with potassium ferricyanide has been reported[1a] to yield a stable 2,6-di-*t*-butyl-7,7-dimethylquinonemethide. Similarly, the corresponding quinonemethides[1a,c] have been prepared from 2,6-di-*t*-butyl-4-(2-butyl)phenol and 2,6-di-*t*-butyl-4-ethylphenol. Apparently the replacement of the hydrogens on C-7 of the quinonemethide with other substituents inhibits the dimerization reaction. In the case of I, the presence of highly electronegative cyano groups imparts considerable stability to the quinonemethide structure.

The reaction of anthrone with thionyl chloride followed by treatment with malononitrile in *p*-dioxane has been reported[2] to produce 10-dicyanomethyleneanthrone (II). In view of the facile interconversion of anthrone and 9-anthrol, it appeared to us that this reaction, if applicable to simple phenols, would lead to a synthesis of 7,7-dicyanoquinonemethides. Thus, I was obtained by the reaction of 2,6-dimethylphenol, thionyl chloride, and malononitrile.

In contrast to the high yield (88%) of II obtained with anthrone, the use of 2,6-dimethylphenol *via* a similar sequence of reactions resulted in a low yield of the quinonemethide I. This compound was isolated from the reaction of the above phenol with thionyl chloride and malononitrile as a dark red complex formed between the quinonemethide I and 2,6-dimethyl-4-chlorophenol. The chlorophenol was formed by the action of thionyl chloride on 2,6-dimethylphenol. Considerable difficulty was encountered in consistently obtaining the product. The reaction was always accompanied by considerable tar formation. In addition to the quinonemethide, one or more of the following compounds were isolated from different runs: 2,6-dimethyl-4-chlorophenol, sulfur, tetracyanoethylene, 2,6-dimethyl-4-tricyanovinylphenol, bis(3,5-dimethyl-4-hydroxyphenyl)malononitrile, and 3,5-dimethyl-4-hydroxyphenyl 3,5-dimethyl-4-hydroxybenzenethiolsulfonate.[3]

In view of the high reactivity of *p*-benzoquinonemethides, perhaps the low yield of I is not unreasonable. In fact it is somewhat surprising that it was isolated from the reaction mixture which at one time contained thionyl chloride, hydrogen chloride, malononitrile, etc. The addition of 2,6-dimethyl-4-chlorophenol to the initial mixture to increase the chlorophenol available for complexing failed to result in a higher yield of I. Neither this chlorophenol nor tetracyanoethylene appeared to be an intermediate in the reactions leading to the synthesis of I. Although we feel that the quinonemethide formation is proceeding *via* the same mechanism as for 10-dicyanomethyleneanthrone synthesis involving a sulfur-containing intermediate, the two paths need not be the same.

The quinonemethide I was readily separated as golden yellow needles by trituration of the red complex with ethanol to remove 2,6-dimethyl-4-chlorophenol. The complex was readily re-formed by the addition of the chlorophenol. In the infrared, I exhibited a sharp absorption band at 2240 and a strong band at 1640 cm.$^{-1}$ characteristic for a conjugated nitrile group and a quinone CO group,[4] respectively. The CO absorption band of I in comparison to the same band in *p*-



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(1) (a) C. D. Cook and B. E. Norcross, *J. Am. Chem. Soc.*, **78**, 3797 (1956); (b) C. D. Cook and B. E. Norcross, *ibid.*, **81**, 1176 (1959); (c) L. Filar and S. Winstein, *Tetrahedron Letters*, **25**, 9 (1960); (d) J. D. McClure, *J. Org. Chem.*, **27**, 2365 (1962); (e) A. Huebele, H. Suhr, and U. Heilmann, *Ber.*, **95**, 639 (1962).

(2) H. H. Takimoto and L. O. Krbechek, *J. Org. Chem.*, **27**, 4688 (1962).

(3) H. H. Takimoto and G. C. Denault, *ibid.*, **29**, 759 (1964).

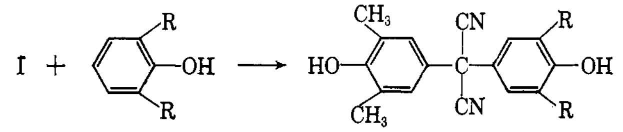
(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapters 9 and 15.

benzoquinone had undergone a shift to a lower frequency. An ultraviolet absorption band at 334 $m\mu$ (ϵ 36,300) taken in ethanol was also observed. The proton n.m.r. spectrum of I in deuteriochloroform showed peaks at 2.52 and 7.71 p.p.m. from tetramethylsilane in the ratio of 3:1.

The quinonemethide I readily underwent a 1,6-addition with 2,6-dimethylphenol in the presence of an acid to yield bis(3,5-dimethyl-4-hydroxyphenyl)malononitrile (III). This compound was also obtained in some runs during the synthesis of I presumably from the reaction of I with 2,6-dimethylphenyl chlorosulfinate in the reaction mixture or from the free phenol formed during the work-up. III was converted to the diacetate IV with acetic anhydride or to the dimethyl ether V with dimethyl sulfate. Hydrolysis and decarboxylation of III gave bis(3,5-dimethyl-4-hydroxyphenyl)-acetic acid (VI). The latter compound was further converted to the ethyl ester VII by ethanolysis. VI was found to be identical with the compound[5] prepared from 2,6-dimethylphenol and diethyl ketomalonate followed by hydrolysis and decarboxylation.

Compound I appears to be similar in its chemical behavior with 7,7,8,8-tetracyanoquinonedimethide.[6] I was reduced to 2,6-dimethyl-4-dicyanomethylphenol in high yield either by catalytic hydrogenation or with thiophenol. Although 10-dicyanomethyleneanthrone, a structural analog of I, was catalytically hydrogenated, attempted reduction using thiophenol failed to yield 10-dicyanomethylanthrone. These results represent another case in which the *p*-benzoquinoid compound was more readily reduced to the aromatic structure than the corresponding anthraquinoid compound. The reduction of I with mercaptoacetic acid gave a low yield of 2,6-dimethyl-4-dicyanomethylphenol, the major product being a sulfur- and a nitrile-containing compound, whose structure as yet has not been identified.

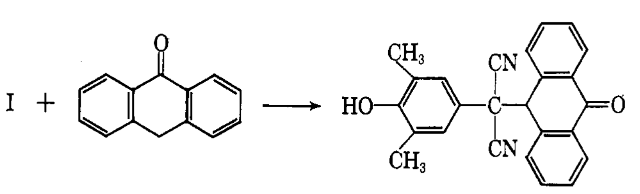
The acid-catalyzed 1,6-addition of phenols to I appears to be a general reaction. In addition to 2,6-dimethylphenol mentioned earlier, I reacted with both phenol, itself, and 2,6-di-*t*-butylphenol to yield the corresponding 3,5-dimethyl-4-hydroxyphenyl malononitrile derivatives VIII where R = H, CH_3, or t-C_4H_9.



VIII

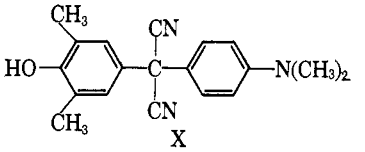
In the absence of an acid, I formed a bright red complex with phenol or 2,6-dimethylphenol, whereas with 2,6-di-*t*-butylphenol, complex formation appeared not to take place. This is probably due to the bulkiness of *t*-butyl groups of the latter compound and may also account for the fact that the di-*t*-butylphenol underwent the addition to I with some reluctance in comparison to other phenols.

Similar to the reactions with phenols, I also reacted with anthrone to yield the 10-anthronylmalononitrile derivative IX. However, the reaction of 10-dicyanomethyleneanthrone (II) with 2,6-dimethylphenol catalyzed by boron trifluoride etherate or hydrogen chloride failed to yield IX under the conditions tried.



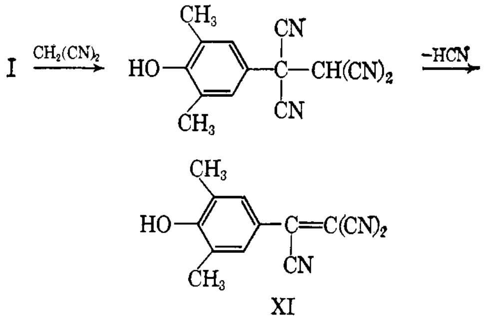
IX

The reaction of I with N,N-dimethylaniline yielded an addition product (X). A structure isomeric to X involving a nuclear substitution of the 4-dimethylanilino group on the quinonemethide ring, although possible, has been ruled out by its nuclear magnetic resonance spectrum.



X

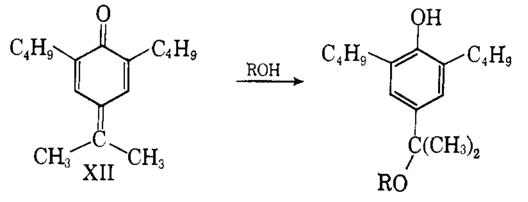
In contrast to the above reaction, the treatment of I with malononitrile in either acid or base yielded 2,6-dimethyl-4-tricyanovinylphenol (XI) which had previously been prepared[7] from 2,6-dimethylphenol and tetracyanoethylene. In the present case XI presumably resulted from the initial addition of malononitrile to I, followed by the elimination of hydrogen cyanide. It can readily be seen that XI found in the synthesis of I probably resulted from this reaction since malononitrile was used in excess.



XI

The treatment of the quinonemethide I with amines such as aniline, piperidine, and pyrrolidine appeared to result in initial formation of intensely colored complexes which reacted further to yield displacement and/or addition products. These products with amines have not been characterized as yet, although with aniline an addition product has been isolated.

The 1,6-addition of alcohol to 2,6-di-*t*-butyl-7,7-dimethylquinonemethide (XII) has been reported[1a] to proceed at room temperature when catalyzed by sulfuric acid. However, a solution of I in methanol con-



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[5] R. V. Smith and M. D. Bealor, *J. Org. Chem.*, **27**, 3092 (1962).

[6] (a) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962); (b) W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. E. Benson, *ibid.*, **84**, 3387 (1962).

[7] G. N. Sauesen, V. A. Engelhardt, and W. J. Middleton, *ibid.*, **80**, 2815 (1958).

taining sulfuric acid yielded the unchanged quinonemethide, even after heating for 0.5 hr. I appears to be considerably less reactive than XII.

Experimental[8,9]

2,6-Dimethyl-7,7-dicyanoquinonemethide (I).—2,6-Dimethylphenol (9.76 g.) was added to 40 ml. of thionyl chloride and the resultant yellow solution was refluxed for 45 min. A vigorous evolution of hydrogen chloride was observed during this heating period. Malononitrile (10.56 g.) dissolved in 120 ml. of *p*-dioxane (distilled from sodium) was then added to the hot solution. Approximately 60 ml. of distillate was then removed from the system under reduced pressure and the remaining solution was refluxed for 1 hr. The solution, which was initially yellow, changed in color to amber, cherry red, and finally dark red to almost black. The remaining thionyl chloride and dioxane were then removed under reduced pressure leaving a black, viscous material. This material was poured out into a beaker and allowed to stand in the open for 2 days. During this time the material had hardened somewhat to a black tarry mass. The black mass was repeatedly extracted with hot petroleum ether (b.p. 60–90°). The dark red petroleum ether extracts were combined and concentrated to yield 4.5 g. of a dark red solid. This red solid was contaminated with free sulfur and 2,6-dimethyl-4-chlorophenol. Repeated recrystallizations from petroleum ether using decolorizing carbon yielded 3.0 g. (22%) of dark red needles melting at 94–96°. This solid proved to be a complex between 2,6-dimethyl-7,7-dicyanoquinonemethide (I) and 2,6-dimethyl-4-chlorophenol.

Anal. Calcd. for $C_{19}H_{17}N_2ClO_2$: C, 66.96; H, 5.03; N, 8.22. Found: C, 67.01; H, 5.01; N, 8.21.

The red complex of 2,6-dimethyl-7,7-dicyanoquinonemethide and 2,6-dimethyl-4-chlorophenol was triturated with small portions of ethanol until a gold colored solid was obtained. This solid was recrystallized from cyclohexane to yield 2,6-dimethyl-7,7-dicyanoquinonemethide as golden needles melting at 134–135°. A molecular weight determination by freezing point depression in benzene gave values of 177 and 172.

Anal. Calcd. for $C_{11}H_8N_2O$: C, 71.72; H, 4.38; N, 15.22. Found: C, 71.91; H, 4.52; N, 15.22.

The black residue from above, after the petroleum ether extraction of the quinonemethide–chlorophenol complex, was extracted further with several portions of hot benzene. The benzene solutions were combined, treated with decolorizing carbon, and concentrated. From this solution in different runs, there were obtained one or several of the following compounds in varying amounts: 2,6-dimethyl-4-chlorophenol, tetracyanoethylene, 2,6-dimethyl-4-tricyanovinylphenol, sulfur, bis(3,5-dimethyl-4-hydroxyphenyl)malononitrile, and 3,5-dimethyl-4-hydroxyphenyl 3,5-dimethyl-4-hydroxybenzenethiolsulfonate.[3]

The above procedure describes a run in which one of the best yields of I was obtained. Even when the apparent identical procedure was followed, the yields varied from 0 to 25%. We have been unable to determine the optimum conditions necessary for consistently obtaining a significant yield. However, the reaction carried out as described above has been satisfactory in providing the quinonemethide for the present study.

Bis(3,5-dimethyl-4-hydroxyphenyl)malononitrile (III).—A gold colored solution of the quinonemethide (0.18 g.) and 2,6-dimethylphenol (0.15 g.) dissolved in 25 ml. of benzene was saturated with gaseous hydrogen chloride, stoppered, and then allowed to stand overnight. The golden solution had turned water white during this time. The benzene solution was concentrated down to give a quantitative yield of a white crystalline solid (III) melting at 196–198°. This product was recrystallized from benzene. The infrared spectrum of the product showed an absorption band at 2530 cm.$^{-1}$ (CN).

Anal. Calcd. for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.22; H, 5.72; N, 9.16.

Bis(3,5-dimethyl-4-acetoxyphenyl)malononitrile (IV).—A mixture of bis(3,5-dimethyl-4-hydroxyphenyl)malononitrile (1.0 g.), pyridine (20 ml.), and acetic anhydride (8 ml.) was refluxed for 2 hr. The reaction mixture was cooled to room temperature and then poured onto crushed ice. The white solid, which precipitated, was separated, washed first with cold 2% hydrochloric acid and then with water, and dried to yield 1.25 g. (98%) of IV. Recrystallizations from ethanol gave white crystals, m.p. 211–214°. The infrared spectrum of the product exhibited absorption bands at 2260 (CN) and 1757 cm.$^{-1}$ (CO_2R).

Anal. Calcd. for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.18. Found: C, 70.70; H, 5.65; N, 7.31.

Bis(3,5-dimethyl-4-methoxyphenyl)malononitrile (V).—A mixture of bis(3,5-dimethyl-4-hydroxyphenyl)malononitrile (3.06 g.), dimethyl sulfate (5 ml.), and potassium carbonate (5.0 g.) in 100 ml. of acetone was refluxed for 19 hr. The mixture was allowed to cool and then filtered. The white solid, obtained after the removal of the solvent, was washed with water and then recrystallized from cyclohexane to yield 3.11 g. (93%) of bis(3,5-dimethyl-4-methoxyphenyl)malononitrile, m.p. 139–142°. Further recrystallizations from cyclohexane yielded an analytical sample, m.p. 142–144°. The infrared spectrum of the product exhibited a nitrile absorption band at 2260 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.37; H, 6.68; N, 8.40.

Bis(3,5-dimethyl-4-hydroxyphenyl)acetic Acid (VI).—A solution of bis(3,5-dimethyl-4-hydroxyphenyl)malononitrile (1.5 g.) and sodium hydroxide (25.0 g.) dissolved in dioxane (30 ml.) and water (75 ml.) was refluxed for 3.5 hr. The color of the solution turned from an initial purple to dark green. An evolution of ammonia was detected during this heating period. The solution was cooled, poured onto crushed ice, and then acidified by a dropwise addition of concentrated hydrochloric acid to the well-stirred cold mixture. The copious precipitate which separated was collected yielding 1.45 g. (98%) of V melting at 209-215°. Recrystallizations from a mixture of toluene and methanol gave white crystals melting at 215–217°. This compound showed no melting point depression when mixed with a sample of bis-(3,5-dimethyl-4-hydroxyphenyl)acetic acid (m.p. 214–216°) prepared by the method of Smith and Bealor[5] and their infrared spectra were identical.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.07; H, 6.76.

Ethyl Bis(3,5-dimethyl-4-hydroxyphenyl)acetate (VII).—A solution of bis(3,5-dimethyl-4-hydroxyphenyl)acetic acid (0.8 g.) in 25 ml. of ethanol and 5 ml. of concentrated hydrochloric acid was refluxed for 24 hr. A quantitative yield of VII separated from the reaction mixture upon cooling to room temperature. An analytical sample, m.p. 164–165°, was prepared by three recrystallizations from benzene. The infrared spectrum of the product showed absorption bands at 3580 (OH) and 1720 cm.$^{-1}$ (CO_2R).

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 73.17; H, 7.25.

2,6-Dimethyl-4-dicyanomethylphenol. A.—A solution of the quinonemethide I (0.40 g.) dissolved in 75 ml. of benzene was hydrogenated for 2 hr. using 0.05 g. of 5% palladium on charcoal. The mixture was filtered and the filtrate was concentrated to about 20 ml. Cyclohexane (20 ml.) was then added and the solution was placed in the cold for 10 min. White crystals which appeared were separated by filtration to yield 0.39 g. (96.5%) of 2,6-dimethyl-4-dicyanomethylphenol melting at 141–143°. Two recrystallizations from benzene–cyclohexane mixture yielded an analytical sample, m.p. 142–144°. The infrared spectrum of the product exhibited absorption bands at 3580 (OH) and 2265 cm.$^{-1}$ (CN). The proton n.m.r. spectrum in deuteriochloroform showed peaks at 2.70 (methyl), 5.15 (hydroxyl), 5.25 (methine), and 7.25 p.p.m. (aromatic) from tetramethylsilane in the ratio of 6:1:1:2, respectively. The hydrogen absorption at 5.15 p.p.m. appeared as an extremely broad peak.

Anal. Calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 71.3; H, 5.46; N, 14.81.

B.—Thiophenol (3 ml.) was added to a solution of the quinonemethide (0.18 g.) in 10 ml. of acetic acid. The gold colored solution turned orange red. After standing overnight at room temperature, the color of the solution had changed to yellow. The volatile materials were then allowed to evaporate leaving a yellow crystalline residue. This residue was only partially soluble in cyclohexane. The white solid insoluble in cold cyclohexane was separated to yield 0.17 g. (93.5%) of 2,6-dimethyl-4-dicyanomethylphenol melting at 139–141°. Mixture

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[8] All melting points are uncorrected.

[9] Analysis were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., Micro-Tech Laboratories, Skokie, Ill., and by Mr. S. Hotta of Aerospace Corp. The infrared and ultraviolet spectra were obtained on a Perkin-Elmer Model 21 and a Beckman DK-2 spectrophotometer. A Varian HR-60 n.m.r. spectrometer was used for the proton n.m.r. spectra.

melting point with the catalytic hydrogenation product of the quinonemethide showed no depression and their infrared spectra were identical.

Reaction of the Quinonemethide with Phenol.—A gold colored solution of the quinonemethide (0.18 g.) and phenol (0.15 g.) dissolved in 20 ml. of tetrahydrofuran containing 5 drops of concentrated hydrochloric acid was allowed to stand at room temperature for 2 days. The volatile materials were then removed from the pale yellow solution leaving a light brown residue. This residue was dissolved in hot benzene. On cooling 3,5-dimethyl-4-hydroxyphenyl-(4-hydroxyphenyl)malononitrile (0.26 g., 96%) separated as light brown needles which melted at 190–194°. Recrystallizations from benzene yielded an analytical sample, m.p. 196–198°. This compound when mixed with bis-(3,5-dimethyl-4-hydroxyphenyl)malononitrile (III) melted at 170–185°. The infrared spectrum of the product exhibited absorption bands at 3460, 3350 (OH), and 2275 cm.$^{-1}$ (CN).

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 73.6; H, 5.14; N, 10.08.

Reaction of the Quinonemethide with 2,6-Di-*t*-butylphenol.—Concentrated hydrochloric acid (5 drops) was added to a solution of the quinonemethide (0.18 g.) and 2,6-di-*t*-butylphenol (0.25 g.) in 25 ml. of tetrahydrofuran. The gold colored solution was allowed to stand at room temperature for 24 hr. No color change was observed. The removed of the volatile constituents gave impure starting materials as the residue. Tetrahydrofuran (25 ml.) and concentrated hydrochloric acid (5 drops) were again added. Refluxing the golden solution for 3 hr. effected no change in color. Five more drops of concentrated hydrochloric acid were added and the stoppered flask was set aside. After 3 days the golden color had disappeared. The removal of the volatiles yielded 0.26 g. (66.5%) of 3,5-dimethyl-4-hydroxyphenyl-(3,5-di-*t*-butyl-4-hydroxyphenyl)malononitrile melting at 171–175°. Recrystallizations from cyclohexane yielded an analytical sample, m.p. 176.5–178°. The infrared spectrum of the product showed absorption bands at 3570 (OH) and 2270 cm.$^{-1}$ (CN).

Anal. Calcd. for $C_{25}H_{30}N_2O_2$: C, 76.89; H, 7.74; N, 7.18. Found: C, 76.6; H, 8.00; N, 7.33.

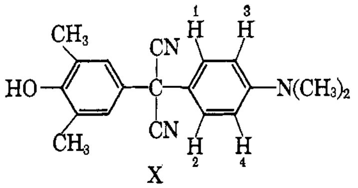
Reaction of the Quinonemethide with Anthrone.—A solution of the quinonemethide (0.18 g.) and anthrone (0.20 g.) in 20 ml. of tetrahydrofuran containing 5 drops of concentrated hydrochloric acid was allowed to stand for 3 hr. During this time the gold colored solution gradually turned yellow and white crystals separated out from the reaction mixture. The mixture was concentrated and then cooled to yield 0.36 g. (95%) of 3,5-dimethyl-4-hydroxyphenyl(10-anthronyl)malononitrile. Two recrystallizations from acetonitrile gave 0.32 g. of a white solid melting at 258–261°. The infrared spectrum of the product showed absorption bands at 3360 (OH), 2265 (CN), and 1670 cm.$^{-1}$ (quinone CO).

Anal. Calcd. for $C_{25}H_{18}N_2O_2$: C, 79.35; H, 4.80; N, 7.40. Found: C, 79.5; H, 4.81; N, 7.17.

Reaction of the Quinonemethide with N,N-Dimethylaniline.—Acetic acid (1 ml.) was added to a dark blue solution of the quinonemethide (0.18 g.) and N,N-dimethylaniline (1 ml.) dissolved in 10 ml. of tetrahydrofuran and the resultant solution was gently warmed for 1 hr. The dark solution was cooled and 25 ml. of water was added. White needles (0.30 g.) which separated were collected. An analytical sample (m.p. 157–158°) of 3,5-dimethyl-4-hydroxyphenyl-(4-N,N-dimethylanilino)malononitrile (X) was prepared by recrystallizations from cyclohexane. Infrared spectrum of the product showed absorption bands at 3600 (OH) and 2260 cm.$^{-1}$ (CN).

Anal. Calcd. for $C_{19}H_{19}N_3O$: C, 74.71; H, 6.27; N, 13.76. Found: C, 74.90; H, 6.35; N, 13.89.

The proton n.m.r. spectrum in deuteriochloroform showed peaks at 2.56 (methyl), 3.26 (methyl), 4.95 (hydroxyl), and 7.22 p.p.m. (aromatic) from tetramethylsilane in the ratio of 6:6:1:2, respectively. In addition the protons at positions 1, 2, 3, and 4



X

gave rise to a set of four lines at 6.74, 7.00, 7.34, and 7.39 p.p.m. corresponding to an AB-type spectrum. This indicated that positions 1 and 2 are equivalent but chemically shifted from the other equivalent protons at positions 3 and 4. The sum of the areas under each pair of lines corresponded to two protons.

In the absence of an acid catalyst, the quinonemethide and N,N-dimethylaniline yielded a complex which was isolated as dark blue shiny crystals. The complex was decomposed readily giving back the original quinonemethide on standing in the open at room temperature or on a melting point block at about 60°.

Reaction of the Quinonemethide with Malononitrile.—A solution of the quinonemethide (0.18 g.) and malononitrile (0.07 g.) dissolved in 10 ml. of tetrahydrofuran containing 5 drops of concentrated hydrochloric acid was allowed to stand at room temperature for 16 hr. Upon removal of the solvent, a quantitative yield of 2,6-dimethyl-4-tricyanovinylphenol, m.p. 178–181°, was obtained. Several recrystallizations from benzene gave a sample melting at 182–183° dec. This compound showed no melting point depression when mixed with an authentic sample of 2,6-dimethyl-4-tricyanovinylphenol[6] prepared by the reaction of 2,6-dimethylphenol with tetracyanoethylene. The infrared spectra were identical.

Anal. Calcd. for $C_{13}H_9N_3O$: C, 69.94; H, 4.07; N, 18.82. Found: C, 70.2; H, 4.16; N, 18.92.

The same product, 2,6-dimethyl-4-tricyanovinylphenol, was obtained from the reaction between the quinonemethide and malononitrile with pyridine and also in the absence of any catalyst.

Acknowledgment.—The authors are grateful to Dr. A. G. Whittaker for measurements and interpretations of nuclear magnetic resonance spectra. The authors are also indebted to Dr. L. Schieler for the helpful interest in this work and to Mr. S. Hotta for infrared and ultraviolet spectral measurements and assistance in the laboratory.