Anal. Calcd. for $C_{48}H_{42}O_2Si_4$: Si, 14.71. Found: Si, 14.50, 14.51.

Similarly, hydrolysis of 1,5-dichlorodecaphenylpentasilane (19.2 g.) in tetrahydrofuran (150 ml.) using 80 ml. of 0.1 *N* hydrochloric acid gave 1,5-dihydroxydecaphenylpentasilane, 17.05 g. (92.2%); m.p. after recrystallization from cyclohexane and benzene, 172–174°; m.m.p. with an authentic specimen, 171–174°. Additional identification of the product was obtained from the superimposability of the infrared spectra.

1,4-Dihydroxyoctaphenyltetrasilane on an Alumina Column.—1,4-Dihydroxyoctaphenyltetrasilane (1.45 g.) was placed on an alumina column. Elution with successive portions of petroleum ether (b.p. 50–60°), carbon tetrachloride, benzene, and ethyl acetate gave 0.32 g. (46%) of *sym*-tetraphenyldisilane, m.p. 76–78°, and 0.02 g. (4%) of octaphenylcyclotetrasiloxane, m.p. 184–185°, identified by mixture melting point and infrared spectra.

Treatment of 1,4-Dihydroxyoctaphenyltetrasilane with Hydrochloric Acid.—1,4-Dihydroxyoctaphenyltetrasilane (3.0 g.) in 10 ml. of ether was treated with 10 ml. of 6 *N* hydrochloric acid solution for 2 hr. The ether layer was separated and evaporated to yield a solid, m.p. 198–200°, which had an infrared spectrum identical with that of the starting material and contained no bands due to Si–H and Si–O–Si.

1,5-Dihydroxydecaphenylpentasilane on an Alumina Column.—1,5-Dihydroxydecaphenylpentasilane (23.7 g.) was dissolved in benzene and placed on an alumina column 16 in. high and 2 in. in diameter. Fractions were eluted with benzene and, subsequent to recrystallization from acetone and methanol, gave 1,1,2,2,3,3-hexaphenyltrisilane, 8.54 g. (62.1%), m.p. 95–97°; m.m.p. with an authentic specimen, 95–97°.

In a second run, 1,5-dihydroxydecaphenylpentasilane (5.7 g.) was placed on an alumina column and eluted with benzene, to give 0.4 g. of a solid, m.p. 97–98°. This had the same infrared spectrum as the 1,1,2,2,3,3-hexaphenyltrisilane isolated from the chromatography of 1,1,2,2,3,3,4,4-octaphenyltetrasilane-1-ol. There was no depression of the melting point of a mixture of the two products. Ethyl acetate elutions afforded 1.9 g. of a mixture of 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol, m.p. 180–181° (identified by mixture melting point and infrared spectrum); and also some of the starting material (infrared).

1,5-Dichlorodecaphenylpentasilane on an Alumina Column.—1,5-Dichlorodecaphenyl pentasilane (29.5 g.) was dissolved in benzene and placed on an alumina column 18 in. high and 2 in. in diameter. Elution of all the fractions with benzene and recrystallization from methanol and acetone gave 8.25 g. (50.0%) of 1,1,2,2,3,3-hexaphenyltrisilane, m.p. 95–97° (mixture melting point with authentic specimen undepressed). The other products were glues which could not be crystallized. The 1,1,2,2,3,3-hexaphenyltrisilane was identified additionally from the superimposability of its infrared spectrum with that of an authentic specimen.

1,1,2,2,3,3,4,4-Octaphenyltetrasilan-1-ol on an Alumina Column.—A solution of 2.7 g. of 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol in 25 ml. of carbon tetrachloride was placed on an alumina column. Carbon tetrachloride and benzene elutions afforded 0.99 g. (51%) of a solid, m.p. 96–98°, which was 1,1,2,2,3,3-hexaphenyltrisilane.

Anal. Calcd. for $C_{36}H_{32}Si_3$: Si, 15.3. Found: Si, 15.40, 15.45.

The infrared spectrum is similar to those of *sym*-tetraphenyl disilane and 1,1,2,2,3,3,4,4-octaphenyltetrasilane, but possesses an Si-H band of intermediate intensity. This trisilane was separated from the starting material, which was also partially eluted, by its solubility in hot petroleum ether (b.p. 50–60°). In the preparatory method for the trisilane, better results were obtained with a long alumina column.

Similarly, 50 g. of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane afforded 18.5 g. (52%) of 1,1,2,2,3,3-hexaphenyltrisilane. This latter reaction appeared to take a longer time than that starting with the corresponding silanol.

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The Structures of Substituted *o*-Quinone Methide Trimers

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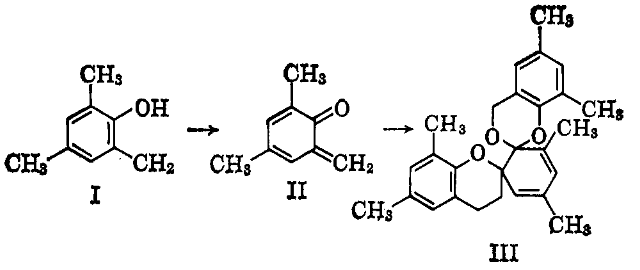
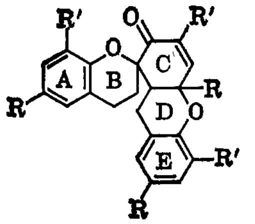
The facility with which substituted *o*-quinone methides dimerize and trimerize was recognized as early as 1907.[1] While a great deal of literature bearing on the structures of trimers has been written, most of it is concerned specifically with the trimer of 3,5-dimethylquinone-(2)-methide (II).[2] No less than three structures have been proposed for this substance. The most recent of these, the "benzodioxan" structure (III), was suggested[3] in 1941 and given additional support more recently.[4,5]



Recent studies on the structure of the trimer of *o*-quinone methide itself led to the assignment shown in IV[2] and prompted a re-examination of the properties of earlier reported substituted trimers. The trimer of 3,5-dimethylquinone-(2)-methide and of 3-chloromethyl-5-methylquinone-(2)-methide were studied as representative cases. Evidence is now presented establishing that these two are related and have a ring system identical with that of the parent (IV). They are, therefore, formulated as V and VI, respectively.



IV, R = R' = H
V, R = R' = CH_3
VI, R = CH_3, R' = CH_2Cl

Although V does not form carbonyl derivatives, the presence of an α,β-unsaturated ketone functionality was suggested by infrared data (ν_{max} 5.91 μ) and confirmed by quantitative microhydrogenation. It absorbed 0.97 mole equivalent of hydrogen to afford a dihydroketone (VII), m.p. 180–181°, ν_{max} 5.81 μ. Further reduction with lithium aluminum hydride

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(1) K. Fries and K. Kann, *Ann.*, **353**, 339 (1907).

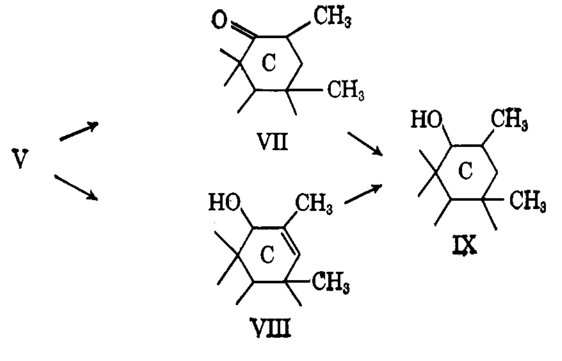
(2) S. B. Cavitt, H. Sarrafizadeh R., and P. D. Gardner, *J. Org. Chem.*, **27**, 1211 (1962), and references cited therein.

(3) G. Schiemann and K. Hultzsch, *Naturwissenschaften*, **35**, 124 (1948).

(4) G. Schiemann, *Rev. fac. sci. univ. Istanbul*, **17A**, 290 (1952); *Chem. Abstr.*, **48**, 3293 (1954).

(5) H. Civelekoglu, *Rev. fac. sci. univ. Istanbul.*, **18A**, 14 (1953); *Chem. Abstr.*, **48**, 5139 (1954).

gave a carbinol (IX), m.p. 133–135°. Alternatively, reduction of V afforded an unsaturated carbinol (VIII), m.p. 145–146°, which in turn gave IX upon hydrogenation. The presence of two benzenoid rings in this product is indicated by its ultraviolet absorption, λ_{max} 280 and 287 mμ; ϵ 3890 and 3840, respectively.



These assignments were corroborated by n.m.r. data. The lone olefinic proton of V was observed at 3.63 τ and identified by comparison with the spectrum of IV. This proton is not strongly coupled indicating the absence of protons on adjacent carbon atoms. The small splitting (J = 1.3 c.p.s.) is due to coupling with the methyl group adjacent to the carbonyl (8.21 τ). The methyl is observed as a doublet and the olefinic proton as a quartet. The methyl group at the bridgehead of rings C and D is at 8.37 τ while three of the aromatic methyls are at 7.83 τ and the fourth at 7.87 τ. The higher field resonance of one aromatic methyl group is thought to be the result of steric repulsion by the bridgehead methyl group, an effect which has been observed with other substances in this laboratory. Additional examples must be examined, however, before it is possible to draw from these data the suggested stereochemical conclusions. The spectrum suggested the absence of protons on carbon atoms adjacent to ethereal oxygen.

The relationship between V and VI was shown by hydrogenation of the latter; the product (VII) was identical with a sample obtained from V.

Experimental

2-Methoxymethyl-4,6-dimethylphenol (I).—The methiodide of 2-dimethylaminomethyl-4,6-dimethylphenol[6] (32.5 g.) was heated under reflux in 200 ml. of 10% methanolic potassium hydroxide for 3 hr. The cooled solution was diluted with a large volume of water and extracted with two portions of ether. The aqueous layer was cooled and acidified whereupon an oily layer separated. It was isolated by several extractions with ether. The combined extracts were washed with saturated aqueous sodium bicarbonate and with water and were then dried with anhydrous sodium sulfate. Freeing of solvent at an aspirator and distillation of the residue through a short column gave 7.35 g. (44%) of 2-methoxymethyl-4,6-dimethylphenol (I), b.p. 46° (0.1 mm.).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.34; H, 8.57.

3,5-Dimethylquinone-(2)-methide Trimer (V).—The pyrolysis system employed was that described for the preparation of the parent trimer (IV).[2] Conditions used were those described. The passage of 13.1 g. of 2-methoxymethyl-4,6-dimethylphenol through the 0.9-cm. tube at 800–850° with nitrogen as a diluent gave crystalline material in the cold receiver as well as in the lower portion of the tube. This combined pyrolysate was recrystallized from ethyl acetate–petroleum ether to give 6.4 g. (60%) of colorless solid, m.p. 199–201°. This material was shown to be identical with that obtained from 2-chloromethyl-4,6-dimethylphenol[1] by means of the usual comparisons. This substance exhibits ultraviolet absorption at 206, 221, and 281 mμ with extinction coefficients 63,000, 21,700, and 2910, respectively. Carbonyl absorption in the infrared is at 5.91 μ.

Anal. Calcd. for $C_{27}H_{30}O_3$: C, 80.56; H, 7.51. Found: C, 80.66; H, 7.60.

Hydrogenation of 3,5-Dimethylquinone-(2)-methide Trimer (V).—A solution of 0.109 g. of the trimer in 15 ml. of ethanol was stirred with 0.075 g. of 10% palladium-carbon (pre-saturated) under 1 atm. of hydrogen. Hydrogen uptake ceased at 5.8 ml. (97% for one double bond). The product, isolated in the usual manner, melted at 179–180° without purification. Several recrystallizations from ethyl acetate-petroleum ether gave a pure sample, m.p. 180.0–180.5°. This dihydro trimer (VII) exhibits carbonyl absorption in the infrared at 5.81 μ. Ultraviolet maxima at 280 and 287 mμ have ϵ values 3890 and 3840, respectively. This substance, like its precursor, does not form carbonyl derivatives.

Anal. Calcd. for $C_{27}H_{32}O_3$: C, 80.16; H, 7.97. Found: C, 79.84; H, 7.79.

Lithium Aluminum Hydride Reduction of 3,5-Dimethylquinone-(2)-methide Trimer (V).—A mixture of 1.0 g. of trimer V, 0.095 g. of lithium aluminum hydride and 20 ml. of purified tetrahydrofuran was stirred at room temperature for 24 hr. Excess reductant was destroyed by the cautious addition of water and then dilute hydrochloric acid. The mixture was extracted with ether and the extract washed thoroughly with water. Drying (sodium sulfate) and evaporation of solvent followed by recrystallization of the residue from ethyl acetate-petroleum ether gave 0.70 g. (70%) of colorless carbinol (VIII), m.p. 145–146°. This substance exhibits no carbonyl absorption in the infrared. It absorbs in the ultraviolet at 280 mμ (ϵ 3620).

Anal. Calcd. for $C_{27}H_{32}O_3$: C, 80.16; H, 7.97. Found: C, 80.00; H, 7.71.

Tetrahydro-3,5-dimethylquinone-(2)-methide Trimer (IX). (A) **From VII.**—A solution of 0.30 g. of dihydro trimer (VII) and 0.10 g. of lithium aluminum hydride in 20 ml. of tetrahydrofuran was stirred at 30° for 12 hr. Moist ether was slowly added followed by dilute hydrochloric acid. The usual isolation by ether extraction and processing of the extract gave a viscous gum. Chromatography (alumina) of a benzene solution of the product afforded crystalline material. Two recrystallizations from petroleum ether gave 0.080 g. (27%) of IX, m.p. 133.5–135.0°. The infrared spectrum of this substance exhibits no absorption in the carbonyl region.

Anal. Calcd. for $C_{27}H_{34}O_3$: C, 79.76; H, 8.43. Found: C, 79.33; H, 8.27.

(B) **From VIII.**—A solution of 0.35 g. of trimer carbinol (VIII) in 40 ml. of ethanol was shaken with 0.20 g. of 10% palladium-carbon under 1 atm. of hydrogen. When hydrogen was no longer absorbed, the catalyst was removed by filtration and the product isolated by evaporation of solvent. Three recrystallizations from petroleum ether afforded 0.115 g. (33%) of IX, m.p. and m.m.p. 133.5–134.0°. The infrared spectrum is identical with that of material prepared from VII.

Reduction of 3-Chloromethyl-5-methylquinone-(2)-methide Trimer (VI).—The chloro trimer (VI, 6.0 g.)[7] in 100 ml. of ethyl acetate was shaken with 5.05 g. of triethylamine and 1.0 g. of 10% palladium-carbon under 3 atm. of hydrogen. When hydrogen uptake ceased, the mixture was processed as described before to give a solid product. Recrystallization from ethanol-petroleum ether afforded 3.0 g. (64%) of VII, m.p. 177–178°. A mixture melting point determination and a comparison of spectra established the identity of this product.

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(6) P. D. Gardner, H. S. Rafsanjani, and L. Rand, *J. Am. Chem. Soc.*, **81**, 3364 (1959).

(7) K. Hultzsch, *J. prakt. Chem.*, **159**, 180 (1941).