

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

UNIVALENT OXYGEN. PREPARATION AND OXIDATION OF MESITOL.

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When Gomberg isolated triphenyl-methyl and produced evidence that other radicals are capable of independent existence,¹ he revived the hopes expressed by Dumas, Kolbe and Frankland, and gave a new impetus to research in organic chemistry. At the present time several compounds of trivalent carbon are known; but with the exception of Kohler's triphenyl-indyl² they all belong to the triarylmethyl class. The search for new types of radicals, and especially those representing unsaturated conditions in elements other than carbon has not been very successful except in the discovery of compounds of divalent nitrogen derived from hydrazine and carbazole. Wieland found that tetra-anisyl hydrazine in benzene has an abnormally low molecular weight; develops a color which deviates from Beer's dilution law; and forms an addition product with nitric oxide. One or two other substituted hydrazines displayed similar properties.³ Branch and Smith obtained a derivative of carbazole which dissociates into radicals of divalent nitrogen.⁴

Porter and Borgstrom prepared tetraphenyl-diarsine⁵ and corresponding derivatives of phosphorus and although these products absorbed oxygen from the air and exhibited other evidences of unsaturation, their properties could be accounted for without assuming any measurable dissociation.

A lead compound bis (lead triphenyl), $(C_6H_5)_3Pb-Pb(C_6H_5)_3$, acquires a color when heated but gives no other evidence of change in structure, and the corresponding derivative of silicon does not dissociate at all.⁶

An attempt to isolate an oxygen radical was made by Pummerer,⁷ who oxidized several naphthol derivatives with potassium ferricyanide and other reagents, thus obtaining tautomeric products corresponding in composition to the original naphthols (or to the peroxides derived from them). Some of these bodies gave colored solutions deviating from Beer's law; and the molecular weights were lower than the calculated values for peroxides. The many possible intramolecular rearrangements, however, made uncertain any deductions with respect to the structures of these oxidation products.

¹ Gomberg, *Ber.*, **35**, 3915 (1902).

² Kohler, *Am. Chem. J.*, **40**, 217 (1908).

³ Wieland, *Ber.*, **45**, 2601 (1912).

⁴ Branch and Smith, *THIS JOURNAL*, **42**, 2405 (1920).

⁵ Porter and Borgstrom, *ibid.*, **41**, 2048 (1919).

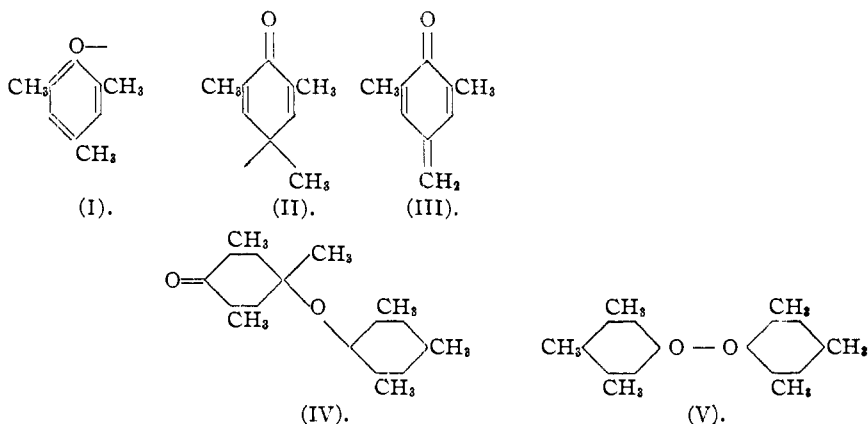
⁶ Schlenk, *Ber.*, **44**, 1179 (1909).

⁷ Pummerer, *ibid.*, **47**, 1472 (1914); Pummerer and Cherbuliez, *ibid.*, **47**, 2957 (1914).

Hunter and Woollett¹ have expressed the opinion that the complex amorphous oxides which they obtained from trihalogenated phenol salts are condensation products of residues containing univalent oxygen; and that in the process of building up these massive structures some of the oxygen valences remain free.

In our work, which has been in progress during the past two years, the aim has been to eliminate some of the possibilities for intramolecular rearrangements, and particularly the shift of a group from phenol oxygen to an *ortho*- or *para*-carbon; to accomplish this we worked with a simple phenol, mesitol, (2,4,6-trimethylphenol), in which the positions *ortho* and *para* to the hydroxyl are occupied by methyl groups.

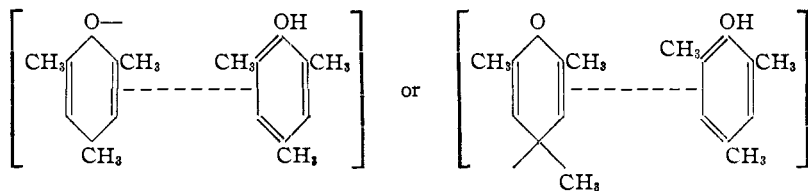
The compound was oxidized by silver oxide and from a mixture of oxidation products we obtained a red crystalline compound melting at 224° to 226°. It has the composition of the peroxide we hoped to obtain; its reactions, however, indicate that it is a quinhydrone. The following formulas represent possible structures of the primary oxidation product.



Formulas I, II and III are excluded, for the molecular weight of the product is above 225, whereas these formulas represent compounds having the molecular weight 135. Moreover, the quantity of any reducing agent required to discharge the red color of a solution of the compound is only half the amount theoretically necessary to reduce I or II and only one-fourth the amount required for Formula III. Formulas IV and V are also unsatisfactory, for, although they are in fair agreement with the determined molecular weight, their complete reduction would require the same quantity of reducing agent per gram of substance as required by Formula I or II. We believe the red crystals represent a quinhydrone composed of equimolecular quantities of unoxidized mesitol and an oxidation product corresponding to Formula I or II. The nature of the union

¹ Hunter and Woollett, *THIS JOURNAL*, 43, 142 (1921).

between the two nuclei is unknown, but may be similar to that existing between quinone and hydroquinone in the ordinary quinhydrone formed when hydroquinone is oxidized. Until further evidence is secured its structure may be represented as:



Regardless of the nature of the tie between the two nuclei it is evident that the compound contains an odd or unpaired electron—the outstanding characteristic of a free radical¹—for it is reduced by the addition of only one hydrogen atom per mol of the compound. It represents therefore an addition to the very limited number of known types of odd molecules. Several years ago, G. N. Lewis suggested that such compounds should be capable of independent existence. To quote his words, “If proper protection against intramolecular rearrangement be provided, we may predict that di-aryl substituted hydrogen peroxide will be prepared, which in turn will dissociate into mono-aryl oxide, ArO, the odd molecule, or free radical, of univalent oxygen.”²

Our oxidation product crystallizes in fine red needles and in benzene forms a deep red colored solution containing less than 0.1% of the solute. It is even less soluble in alcohol and insoluble in water. It is rapidly reduced to colorless products by an alcoholic solution of potassium or sodium hydroxide, but is fairly stable in a very dilute acid solution of alcohol. Stannous chloride, titanous chloride and ferrous sulfate rapidly discharge the color of an alcohol solution of the compound, the original color being restored by treatment with silver oxide. The quantity of any reducing agent required to discharge the color corresponds to the calculated value for the quinhydrone formula or half the quantity required for Formulas I, II, IV, or V. The crystals dissolve in conc. sulfuric acid, giving a very deep red solution, the color of which is discharged by diluting with water. Nitric acid converts it at once into colorless products. These colorless products we have not yet identified.

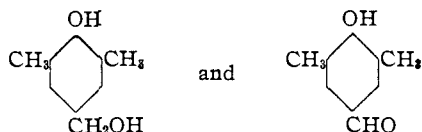
The red compound is totally unlike the oxidation products of mesitol obtained by Bamberger³ and Thiele.⁴ Bamberger used Caro's acid, and Thiele employed amyl nitrite as the oxidizing agent. The formulas assigned to their products are:

¹ Lewis, *THIS JOURNAL*, **38**, 770 (1916).

² Lewis, *Proc. Nat. Acad. Sci.*, **2**, 586 (1916).

³ Bamberger, *Ber.*, **36**, 2030 (1903).

⁴ Thiele and Eichwede, *Ann.*, **311**, 366 (1900).



Both are colorless and water-soluble.

The calculated molecular weight for the quinhydrone is 271. The values we obtained were between 225 and 250. On account of its slight solubility we could not get a freezing-point depression equal to 0.01° and we do not consider the molecular weight determinations sufficiently accurate to justify the conclusion that the low values are due to dissociation. On the other hand, the measurements are good enough to indicate that undissociated molecules contain two mesitol residues.

Experimental.

Preparation of Mesitol.—*Mesidine* (2,4,6-trimethylaniline) was made from 1,2,4-xylylidine and methyl iodide by an application of the Hoffman rearrangement. The success of the method depends upon the purity of the reagents, control of the temperature and the time of heating. Pure 1,2,4-xylylidine was obtained from the mixed isomers (commercial product) by precipitation of the acetate with glacial acetic acid. The crystals were pressed, washed with acetic acid and dried. The free xylylidine was liberated from the crystals by means of sodium hydroxide solution, separated from the water layer and distilled.

Equimolecular quantities of 1,2,4-xylylidine and pure methyl iodide were poured into Pyrex bomb tubes packed in ice. After standing for 2 or 3 hours the tubes, now containing the viscous amber-colored quaternary ammonium compound, were sealed, heated during the course of an hour to 260° , and held at that temperature for three hours.¹ The red waxy or semi-crystalline product was transferred to a flask and neutralized with sodium hydroxide solution. The oily layer, mesidine, was separated and distilled under reduced pressure.

Mesitol.—The mesidine was diazotized in the presence of an excess of dil. hydrochloric acid solution and warmed. Mesitol separated as a red oil. It was removed from the water layer dried with sodium sulfate and distilled under 10 cm. pressure. On standing the distillate crystallized. Recrystallization from 20% alcohol gave pure white feathery crystals melting at 69° .

Oxidation of Mesitol.—Flasks containing 25 g. of moist silver oxide, 5 g. of mesitol and 500 cc. of benzene were sealed and shaken in a thermostat at 50° for 4 hours.

Each solution acquired a deep red color, and a fine red crystalline compound precipitated. On evaporation the filtered solution yielded a small quantity of the red compound, but the major portion was obtained by elutriation from the residual mixture of silver oxide and the red compound remaining in the flask. The crystals are much lighter than the other components of the residue and can be washed out with benzene.

¹ The optimum temperature for the rearrangement seems to be 260° . At temperatures much lower the change does not occur and at higher temperatures there is considerable charring. We used an electric autoclave with a thermoregulator and maintained a temperature that did not vary more than 3° or 4° .

The substance is insoluble in water, and only slightly soluble in alcohol, chloroform and ether. It melts at 224–226°.

Analyses:

Subs. G.	H ₂ O G.	CO ₂ G.	H. %.	C. %.
0.1050	0.0756	0.3113	8.00	80.80
0.1200	0.0853	0.3520	7.90	80.00
0.1425	0.1045	0.4206	8.15	80.50

Calc. for quinhydrone: 8.48, 80.81.

Molecular Weight:

Subs. G.	Cryoscopic method. Solvent, benzene, K=50.		Mol. Wt.
	Solvent. G.	Temp. °C.	
0.0322	100	0.007	230
0.0270	100	0.006	225
0.0900	230	0.008	245
	Calc. for quinhydrone:		271

*Reduction with hydrazine.*¹

Subs. G.	Vol. N ₂ Cc.	Temp. °C.	Barom. Mm.	Wt. N ₂ liberated by 271 G. substance.
0.1105	2.7	15	760	7.72
0.1240	3.1	20	758	7.68
0.1000	2.2	15	760	6.95
	Calc. for quinhydrone:			7.00

Reduction with SnCl₂.

SnCl₂ in dil. HCl standardized by titration with KMnO₄ solution containing 0.5000 g. of KMnO₄ per liter.

10.00 cc. of SnCl₂ ≈ 15.60 cc. of KMnO₄. Subs., 0.03, in 80% alcohol reduced by 4.6 cc. of SnCl₂ solution. Equivalents of reducing agent required for 271 g. of substance = 1.02. Calc. for quinhydrone: 1.00.

Reduction with FeSO₄.

FeSO₄ in dil. H₂SO₄ standardized by titration with KMnO₄ (0.5000 g. per liter). 9.70 cc. of FeSO₄ ≈ 17.05 cc. of KMnO₄. Subs., 0.052 in 80% alcohol reduced by 7.10 cc. of FeSO₄. Equivalents of reducing agent required for 271 g. of substance = 1.03.

Calc. for quinhydrone: 1.00.

Summary.

Mesitol in benzene solution at 50° is oxidized to a red crystalline compound which is unsaturated and is readily reduced to colorless products.

Its molecular weight indicates that it contains two mesitol nuclei.

Its reduction is accomplished by half the quantity of reducing agent that would be required if all the oxygen were quinone or peroxide oxygen.

It is reduced to a saturated product by addition of an uneven number of hydrogen atoms or other electro-chemical equivalents, indicating that it has an impaired or odd electron.

The properties of the compound are accounted for on the basis of a formula containing an oxidized mesitol residue possessing either univalent oxygen or trivalent carbon more or less firmly held by an unoxidized molecule of the phenol.

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¹ Hunter and Woollett, *THIS JOURNAL*, **43**, 138 (1921).