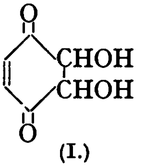
198. *Derivatives of* 1 : 2 : 3 : 4-*Tetrahydroxybenzene. Part VI. The Oxidation of Quinol with Sodium Chlorate.*

By WILSON BAKER and (Miss) I. MUNK.

The substance obtained by oxidising quinol with sodium chlorate in presence of osmium tetroxide is converted by acetic anhydride into 1 : 2 : 3 : 4-tetra-acetoxybenzene. The properties of the oxidation product itself indicate that it is not 2 : 3-dihydroxy-2 : 3-dihydrobenzoquinone (I) as previously suggested, but is probably a dimeride of this compound.

THE oxidation of quinol with aqueous sodium chlorate at room temperature in presence of hydrochloric acid and a trace of osmium tetroxide was studied by Terry and Milas (*J. Amer. Chem. Soc.*, 1926, **48**, 2647), who claim to have isolated a colourless, crystalline compound (decomp. 177—178°) in over 50% yield. These authors suggested that the substance was 2 : 3-dihydroxy-2 : 3-dihydrobenzoquinone (I), largely because on heating with excess of acetic anhydride for 48 hours it yielded a tetra-acetyl derivative, $C_6H_2(OAc)_4$, probably 1 : 2 : 3 : 4-tetra-acetoxybenzene, and was itself clearly not identical with 1 : 2 : 3 : 4-tetrahydroxybenzene (Einhorn, Cobliner, and Pfeiffer, *Ber.*, 1904, **37**, 106). Unfortunately Terry and Milas give no analytical data for their compound, and none of the many experiments carried out allows definite conclusions to be drawn as to its structure. Its molecular weight was determined ebullioscopically in water, and agreed with the formula $C_6H_6O_4$.



(I.)

A number of attempts to prepare the oxidation product of quinol by the method of Terry and Milas were unsuccessful, but after many experiments we succeeded in preparing the compound in 20% yield, but only when about 10 times the amount of osmic acid was employed. We have confirmed the production of the tetra-acetyl derivative, $C_6H_2(OAc)_4$, by prolonged heating with acetic anhydride, but it is much more rapidly obtained by heating with acetic anhydride and anhydrous sodium acetate, and have proved that this substance is, in fact, 1 : 2 : 3 : 4-tetra-acetoxybenzene by simultaneous hydrolysis and methylation, 1 : 2 : 3 : 4-tetramethoxybenzene being obtained.

With regard to the nature of the original oxidation product, analysis establishes the empirical formula $(C_6H_6O_4)_n$, but we have been unable either to crystallise it from any organic solvent or to confirm the statement that the compound can be crystallised from hot water. The substance does dissolve somewhat in boiling water, but does not separate again on cooling or long standing. It is clear that it undergoes change in these circumstances, and hence no value can be attached to the molecular weight determination carried out by Terry and Milas. It rapidly dissolves in dilute alkalis to yellow-brown solutions which stain the skin, but from which the substance is not precipitated on acidification. The alkaline solutions do not yield 1 : 2 : 3 : 4-tetramethoxybenzene on treatment with methyl sulphate. It is insoluble in all organic solvents except bases, in which it dissolves easily, but it cannot be recovered from such solutions. The physical properties of the compound suggest that it is of rather high molecular weight, and we cannot agree with the suggestion of Terry and Milas that it is a simple diketo-form (I) of 1 : 2 : 3 : 4-tetrahydroxybenzene, since, even if these compounds were not actually tautomeric, they should be very similar in physical properties. The fact that the substance is definitely microcrystalline suggests that it is not an indefinite polymer of $C_6H_6O_4$, but is most probably a dimeric form, for which we are not justified in advancing any one of the most likely formulæ.

The expectation that the procedure of Terry and Milas would afford a convenient method for the preparation of derivatives of 1 : 2 : 3 : 4-tetrahydroxybenzene has not been realised, and the best method for the preparation of such compounds remains the oxidation of gallacetophenone 3 : 4-dimethyl ether with alkaline hydrogen peroxide (Baker, Jukes, and Subrahmanyam, J., 1934, 1683; line 3, for " solidified " read " acidified ").

EXPERIMENTAL.

Oxidation of Quinol with Sodium Chlorate and Osmium Tetroxide.—Quinol (10·8 g.) was dissolved in water (180 c.c.), N-hydrochloric acid then added, followed by sodium chlorate (10·8 g.) and a 1% solution of osmium tetroxide (12 c.c.). Immediately on the addition of the osmium tetroxide separation of *p*-benzoquinone and quinhydrone occurred, accompanied by a rise in temperature of some 10°, and the mixture was now shaken for 5 days. It then consisted of a pale yellow solution containing a white microcrystalline deposit, giving a silky appearance on gentle agitation. The solid was collected, thoroughly washed with water, then alcohol, and dried at 120° in a vacuum over potassium hydroxide (yield, 1·34 g.) [Found : C, 50·7; H, 4·2. $(C_6H_6O_4)_n$ requires C, 50·7; H, 4·2%]. Owing to decomposition the m. p. of this product varies between 155° and 185° according to the rate of heating. As ordinarily determined, the substance melts and decomposes between 175° and 180°, but it starts to sinter and darken at about 155°. When rapidly heated, it darkens and melts at about 185°. The original filtrate was concentrated to 80 c.c. under diminished pressure at about 40°, and on standing a greyish crystalline crust was deposited. This was collected, washed, and dried (yield, 1·55 g.) and was identical in all its properties, including its conversion into 1 : 2 : 3 : 4-tetra-acetoxybenzene (below), with the material previously isolated. The total yield of the compound (2·89 g.) is 20% of the theoretical.

1 : 2 : 3 : 4-*Tetra-acetoxybenzene.*—The preceding compound (0·4 g.) was refluxed for 3 hours with acetic anhydride (5 c.c.) and anhydrous sodium acetate (0·5 g.), the solution shaken with water, and the resulting solid collected, washed, and crystallised twice from alcohol. It formed colourless needles, m. p. 134—136° [Found : C, 54·2; H, 4·5; Ac, 51·6. Calc. for $C_6H_2(OAc)_4$: C, 54·2; H, 4·5; Ac, 55·5%] (Einhorn, Cobliner, and Pfeiffer, *loc. cit.*, record m. p. 136°). The oxidation product dissolved only very slowly in boiling acetic anhydride, and at 100° the reaction took 3 days for completion. At the b. p., however, the addition of anhydrous sodium acetate caused almost immediate solution of the compound with development of a pinkish colour.

1 : 2 : 3 : 4-*Tetramethoxybenzene.*—The 1 : 2 : 3 : 4-tetra-acetoxybenzene prepared above was subjected to simultaneous hydrolysis and methylation by shaking and warming in aqueous alcohol with methyl sulphate and 20% potassium hydroxide solution, the mixture being finally diluted with excess of alkali, and the alcohol removed by distillation. The resulting solid separated from light petroleum (b. p. 60—80°) in prisms, m. p. 84—85°. Its m. p. on admixture with 1 : 2 : 3 : 4-tetramethoxybenzene (m. p. 85—86°) was 84—86° and the mixture solidified immediately on cooling.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

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