

A COMPOUND OF 2:6-DIMETHOXY QUINONE AND ACETONE

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IN an earlier publication,¹ a brief study of the methylation of hydroxy quinones was made. It was noticed that even under mild conditions using methyl sulphate, potassium carbonate and acetone the quinones underwent reduction (by dismutation) and subsequent methylation giving rise to the methyl ethers of corresponding quinols. When 2:6-dimethoxy quinone (I) is used in these experiments the result is different and an unexpected new product is formed which has now been studied in detail. Instead of the usual dismutation and methylation leading to the expected tetramethoxy benzene, the product is found to have very different properties. It is a colourless substance melting at 158–59°, readily soluble in water and has a sweet taste. It gives no colour with ferric chloride solution. Analysis for carbon and hydrogen and molecular weight determination indicate that it has resulted simply by the addition of an acetone molecule with a molecule of 2:6-dimethoxy quinone. Later experiments have shown that it could be more conveniently obtained by heating a solution of the quinone in acetone in presence of anhydrous potassium carbonate or by adding absolute alcoholic potash to a suspension of the quinone in acetone. The product is unstable in presence of moisture; even when heated in benzene solution for a long time, or as solid at its melting point for a short time, it decomposes into the original quinone and acetone. This decomposition is much faster in alkaline solution but the resulting quinone undergoes further changes whereas the acetone can be recovered.

The new compound gives definite derivatives for the presence of an alcoholic hydroxyl group (acetylation and benzylation) and for a carbonyl group (2:4-dinitro phenyl hydrazone and semi-carbazone). It also gives the iodoform reaction. It however does not undergo methylation. The analysis of these derivatives again supports the formula of the substance as an addition product. In suggesting a constitution for it, the following possibilities have to be considered:

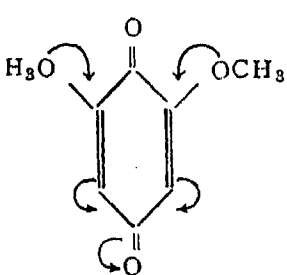
1:4-Addition.—This is quite common with *p*-benzoquinones giving rise to the corresponding quinol derivatives. But this characteristic quinone property is considerably affected by substitution.² 2:6-Dimethoxy quinone is known to be an extremely inert substance towards Thiele mixture and

hydrogen chloride. This inertness has been attributed³ partly to the result of neutralisation of the 4-carbonyl group by both the methoxyls (formula I) diminishing unsaturation in the nuclear double bonds and making the katio-noid system less reactive and partly to the steric effects. Hence an 1:4-addition in the present case will be improbable. In fact the properties of the addition compound are different from those of 2:6-dimethoxy quinol and are shown in the following table (Table I).

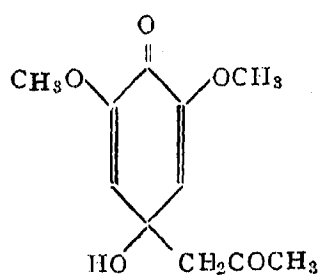
TABLE I

Properties studied	2:6-Dimethoxy quinol	2:6-Dimethoxy quinone-acetone compound
Solubility in water	.. Sparingly soluble	Readily soluble
Sodium hydroxide	.. Intense green solution	The initial colourless solution soon becomes rose red.
Conc. sulphuric acid	.. Deep red solution	Initial brown colour changes to bluish violet.
Methylation	.. Can be readily methylated	Cannot be methylated.
Bromine in chloroform	Gives the crystalline 2:6-dimethoxy-3:5-dibromo quinone	Gives a sticky semi-solid which could not be crystallised.

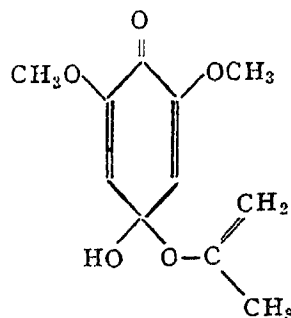
1:2-Addition.—For reasons given in the above para, the diminished activity of the double bond of the ring will lead to removal of conjugation or diminution of conjugation and consequently an increase in the carbonyl activity of the two C = O groups. The more active of the two will be the one in the 4-position since it is sterically free and will have a greater access of electrons for ready co-ordination with protons. Based on these considerations, the following formulæ could be suggested (II and III).



(I)



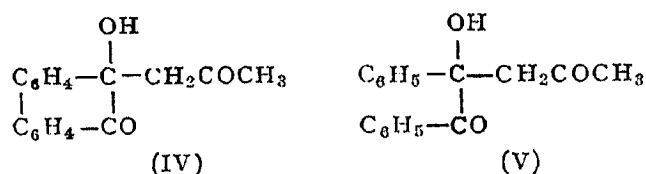
(II)



(III)

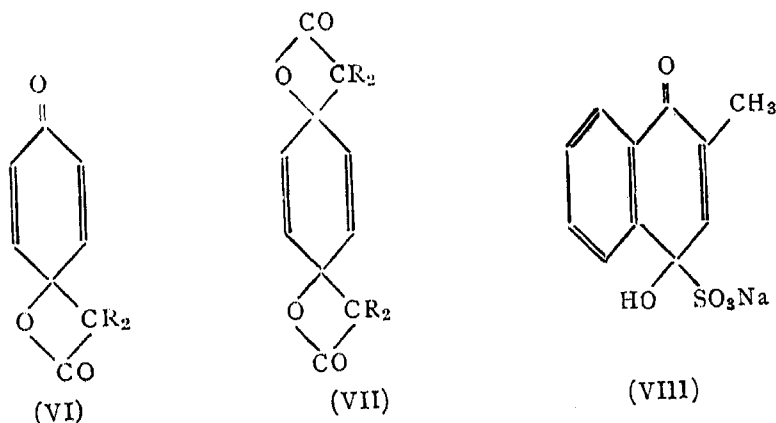
Formula II seems to explain satisfactorily all the properties and reactions of the compound. Particular mention may be made of the ready formation of the 2:4-dinitro phenyl hydrazone. This is readily soluble in aqueous alkali and can be recovered unchanged by acidifying the alkaline solution. The second alternative (III) would attribute the ketonic properties to the quinone carbonyl in position 1, and in analogous cases of pseudoquinols, the reaction with phenyl hydrazine is more complex and yields alkyl azo compounds.⁴

In this connection may be mentioned the earlier study of the addition products of phenanthrenequinone and acetone,⁵ and benzil and acetone⁶ by Japp and co-workers. Phenanthrenequinone reacts with acetone with or without sodium hydroxide as a condensing agent, giving a colourless addition product. The addition product is readily soluble in water and is readily decomposed on heating at its melting point or heating its solution in water, into acetone and phenanthrene quinone. Among the possible formulæ, they considered (IV) as the most probable. Similarly they represented the constitution of the product formed from benzil and acetone as (V).



The above examples are different from 2:6-dimethoxy quinone in that the first is an orthoquinone and the second an α -diketone and they contain two similarly located carbonyl groups whereas in 2:6-dimethoxy quinone one carbonyl is different from the other. Hence the complications⁵ observed in the behaviour of the orthoquinone and benzil are not noticed in the present case. Similar 1:2-addition has been proposed by Staudinger,⁷ for the reaction between diphenyl keten and *p*-benzoquinone. Diphenyl keten reacts with *p*-benzoquinone in the cold giving compounds of the types (VI and VII). These compounds seem to have considerable stability and are decomposed only on very strong heating. More recently it has been noticed,⁸ that *p*-benzoquinone combines with pyridine acetate and formate yielding addition products. It may also be mentioned here that 1:2-addition of sodium bisulphite is considered to take place with menadione to form the water-soluble addition product (VIII).⁹

Among simple *p*-benzoquinones, the combination with acetone seems to be peculiar to 2:6-dimethoxy quinone and obviously the enhanced carbonyl activity of one of the C=O group is necessary. Other quinones like *p*-benzoquinone, and 2:5-dimethoxy-*p*-benzoquinone do not react with



acetone under similar conditions. Methyl ethyl ketone is also found to form an addition product readily with 2:6-dimethoxy quinone.

EXPERIMENTAL

2:6-Dimethoxy-*p*-benzoquinone

For the preparation of this substance in a pure state, the procedure of Baker *et al.*¹⁰ was followed with slight modifications intended to remove effectively the accompanying nitro compound. A typical experiment is described below.

A mixture of pyrogallol trimethyl ether (55 g.), alcohol (275 c.c.) and nitric acid (275 c.c.; d. 1.2) was warmed to 35° and allowed to stand until vigorous reaction set in; the temperature was then kept below 50° for $\frac{1}{4}$ hour. After 4 hours, the quinone was filtered, washed with water (300 c.c.) and then with benzene (200 c.c.). The residue was then almost pure quinone melting at 252–53°, and it was used directly for the experiments described in this paper.

The benzene washings were collected separately and distilled; the residue was filtered and washed with sodium hydroxide solution to remove any of the quinone present. It was then recrystallised from ethanol when it was obtained as colourless stout prisms melting at 109–10°. It was identical with 5-nitro pyrogallol trimethyl ether the m.p. of which however had been reported earlier as 100°. ¹¹ (Found: C, 50.9; H, 5.2; $C_9H_{11}NO_5$ requires C, 50.7; H, 5.2%.) This compound is sparingly soluble in cold alcohol, but is very soluble in cold benzene and hence its removal is efficiently accomplished by washing the mixture with benzene.

Condensation of 2:6-dimethoxy quinone and acetone

(i) *Using anhydrous potassium carbonate.*—A suspension of 2:6-dimethoxy quinone (5 g.) and anhydrous potassium carbonate (5 g.) in dry acetone (100 c.c.) was refluxed for 6 hours. After half an hour the quinone

went into solution. The pale brown reaction mixture was filtered and the potassium salt was washed with hot dry acetone. The combined filtrate and washings were evaporated to dryness. The residue weighing 4 g. was crystallised from a mixture of dry acetone and dry ether. Colourless glistening plates of the addition product melting at 158–59° were obtained.

(ii) *Using alcoholic potassium hydroxide.*—To a suspension of 2:6-dimethoxy quinone (5 g.) in acetone (15 c.c.) was added dropwise absolute alcoholic potassium hydroxide (0.5 c.c.; 10%). The quinone immediately went into solution and the mixture turned deep brown. There was a slight increase in temperature. After 15 minutes the acetone was partially allowed to evaporate in the cold, and benzene (100 c.c.) was added. The brown solid so obtained was filtered, washed with benzene, and immediately recrystallised from acetone-ether mixture. Colourless crystals of the addition product were obtained melting at 158–59°. Yield, 4 g.

Properties of the addition compound

It is sparingly soluble in benzene and ether, but easily in acetone, alcohol and water. It has a mild sweet taste. It does not give any colour with ferric chloride solution. In 5% aqueous sodium hydroxide, the initial colourless solution soon changes to rose red. In concentrated sulphuric acid it forms a deep brown solution which on gentle warming changes into intense bluish violet colour. When an aqueous solution is heated it readily decomposes into acetone and 2:6-dimethoxy quinone. When heated above its melting point it is decomposed into original quinone and acetone. It also gives the iodoform reaction (Found: C, 58.4, 58.6; H, 5.7, 6.6; molecular weight: 216, 227 (depression of freezing point of water); $C_{11}H_{14}O_6$ requires C, 58.4; H, 6.2%; and molecular weight, 226).

Acetate

The addition compound (1 g.) was acetylated by heating with acetic anhydride (5 c.c.) and sodium acetate (1 g.) at 140° for 1 hour. It was then treated with water and the resulting solid was recrystallised from methanol. The acetate came out as colourless needles melting at 127–28° (Found: C, 58.6; H, 6.4; $C_{13}H_{16}O_6$ requires C, 58.2; H, 6.0%).

Benzoate

The addition compound (1 g.) was dissolved in pyridine (15 c.c.) and benzoyl chloride (2 c.c.) was added. The resulting solution was kept at room temperature for 36 hours. It was then treated with water and extracted with ether. The ether solution was washed with ice-cold 2 N hydrochloric acid, then with saturated sodium bicarbonate solution and finally with water

and distilled. The resulting oily liquid was crystallised from petroleum ether when the benzoyl derivative was obtained as long rectangular prisms melting at 52–53°.

2:4-Dinitro phenyl hydrazone

An aqueous solution of the addition compound (1 g.) was treated with a solution of 2:4-dinitrophenyl hydrazine (1 g.) in 4 N hydrochloric acid (25 c.c.). The resulting yellow precipitate was filtered, washed with dilute hydrochloric acid, and water. On recrystallisation from ethyl acetate, it was obtained as bright orange needles melting at 214–15°. The 2:4-dinitro phenyl hydrazone is soluble in aqueous sodium hydroxide producing a deep green solution, and is reprecipitated on the addition of acid (Found: C, 50.6; H, 4.8; $C_{17}H_{18}O_8N_4$ requires, C, 50.2; H, 4.4%).

Semicarbazone

The addition compound (1 g.) was dissolved in water and treated with semicarbazide hydrochloride (1 g.) and sodium acetate (1 g.) heated to boiling, cooled and the resulting solid was recrystallised from alcohol. The semicarbazone was obtained as colourless prisms melting at 200–01°.

Acetone estimation

When an aqueous solution of the addition compound was treated with ammonia and iodine in potassium iodide, a yellow solid was obtained. The identity of the substance with iodoform was confirmed by comparing smell, colour and melting point. But the direct treatment cannot be used for the estimation of acetone in the compound since 2:6-dimethoxy quinone also yields some iodoform by similar treatment. Booth and Saunders¹² have observed that quinones in general give the iodoform reaction.

For estimating the acetone the following procedure was adopted. A known quantity of the addition compound was treated with sodium hydroxide solution and distilled. The liberated acetone was condensed and estimated according to the method of Houghton.¹³ The percentage of acetone in the compound was found to be 21. $C_{11}H_{14}O_5$ requires acetone 25.7%. The low result seems to be due to the low recovery of acetone in the distillation process.

Condensation of 2:6-dimethoxy quinone with methyl ethyl ketone

Methyl ethyl ketone condensed with 2:6-dimethoxy quinone under the same conditions as acetone and gave a colourless substance melting at 131–32°. Its reactions and properties are similar to those of the acetone compound (Found: C, 60.4; H, 7.1; $C_{12}H_{16}O_5$ requires C, 60.0; H, 6.7%).

SUMMARY

In the presence of potassium carbonate or potash, acetone forms an addition product with 2:6-dimethoxy quinone. Its properties and reactions are described. They give evidence for the presence of an aliphatic hydroxyl group and a ketone carbonyl. The combination is considered to involve addition of the acetone molecule at the $C=O$ group in the 4-position of the quinone. Methyl ethyl ketone also forms a similar addition compound. Other simple *p*-benzoquinones do not give this type of compounds.

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