

On the Reactivity of 2,5- and 2,6-Dimethoxyquinone

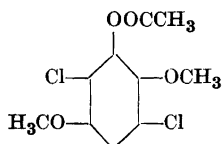
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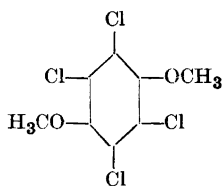
On the addition of hydrogen chloride to 4,4'-dimethoxydiquinone, Erdtman¹ obtained a substance with rather unexpected properties. Quinones generally yield stable monochloro quinols by this reaction, but in the case of 4,4'-dimethoxydiquinone the reaction was reversible and the substance, on attempted recrystallization, decomposed into the original materials. As mentioned in a previous paper², we have started a reinvestigation of the addition product.

The Thiele acetylation of 4,4'-dimethoxydiquinone is a very slow reaction¹. Setting out from this fact, we have assumed as a hypothesis that the halogen quinols are stable when the corresponding quinones react easily with acid reagents, and vice versa. 2,5- and 2,6-dimethoxyquinone are quite stable towards both the Thiele reagent and hydrogen chloride. One might therefore expect that the corresponding monohalogen quinols would be very unstable compounds. In order to obtain the acetates of these substances we have treated the quinones with acetyl chloride and acetyl bromide.

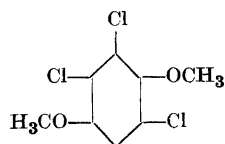
2,5-Dimethoxyquinone did not react with acetyl chloride alone. When sulfuric acid was added, however, the quinone was slowly dissolved. From the reaction mixture considerable amounts of a substance of m. p. 90—91°* could be isolated. This proved to be identical with the dimethoxydichlorophenol acetate which Oliverio³ obtained by treating this quinone with acetyl chloride and aluminium chloride as a catalyst. Oliverio and Castelfranchi⁴ have since shown that the substance is 2,5-dimethoxy-3,6-dichlorophenol acetate (I).



I



II



III

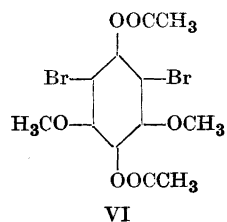
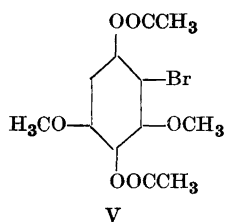
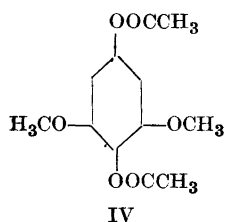
* All melting points uncorrected.

Oliverio also found tetrachloroquinol dimethyl ether (II) in a small amount in his reaction mixture. We have not been able to isolate this substance but could isolate small amounts of trichloroquinol dimethyl ether (III) from our reaction mixture. The two reactions are analogous; the aluminium chloride and the sulfuric acid both being strong acids which catalyze the reaction. Our reaction products (I) and (III) have the same degree of oxidation as the 2,5-dimethoxyquinone, but the mechanism of the reaction is difficult to interpret.

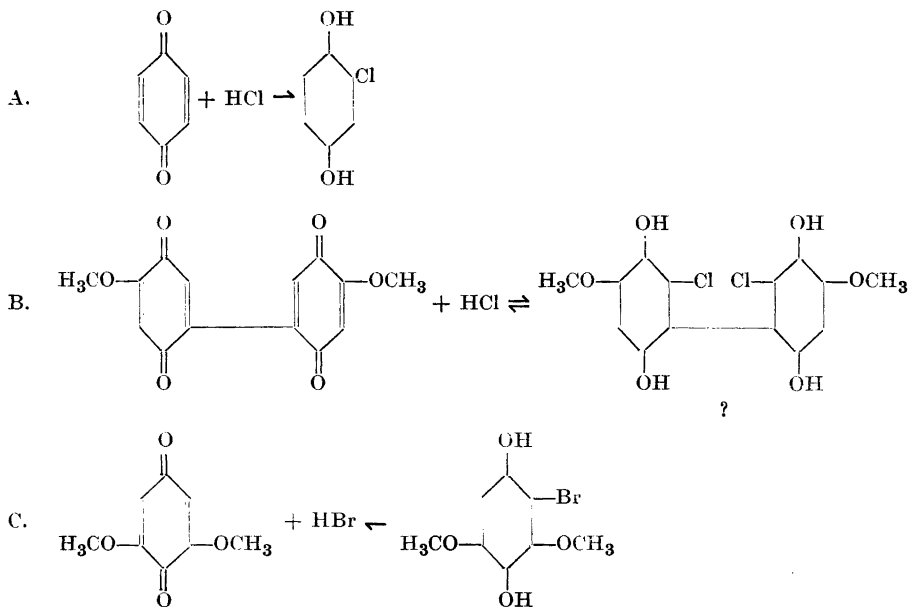
When treated with acetyl bromide, 2,5-dimethoxyquinone was reduced to 2,5-dimethoxyquinol diacetate and bromine was liberated.

2,6-Dimethoxyquinone did not react with acetyl chloride, even when sulfuric acid was added. This is in agreement with the observations of Oliverio ³, who found that this quinone did not react with acetyl chloride in the presence of aluminium chloride.

2,6-Dimethoxyquinone dissolved completely in acetyl bromide. The reaction was accelerated by small amounts of mercuric bromide. From the reaction mixture the unsubstituted (IV), the monobromo (V) and the dibromo-2,6-dimethoxyquinol diacetate (VI) could be isolated. Perhaps the primary reaction here is also reductive acetylation with formation of bromine, but this quinol diacetate is more easily brominated than the isomer mentioned above.



The monobromo derivative, which has not been described before, was also synthesized by reductive acetylation of monobromo-2,6-dimethoxyquinone. On attempted hydrolysis with sulfuric acid in methanol, the intermediate quinol lost hydrogen bromide and gave 2,6-dimethoxyquinone. The monobromo-2,6-dimethoxyquinol could be obtained in ether solution by reducing the monobromoquinone with zinc dust in acetic acid, diluting with water and extracting with ether. (See under Experimental.) However, on concentrating, even under reduced pressure, the substance decomposed. The corresponding dibromoquinol, prepared by Aulin and Erdtman ⁵, is a quite stable compound.



With these experiments the existence of the reverse reaction (C) of the hydrogen halogenide addition to quinones (A) has been demonstrated. The reversibility of the reaction between 4,4'-dimethoxydiquinone and hydrogen chloride (B) is therefore not inconsistent with the assumption that the addition product is a diquinol. This assumption is rather probable when one considers that the reactivity of 4,4'-dimethoxyquinone is between that of the majority of easily reacting quinones and those completely unreactive. The fact that the addition product yields a diacetate and not a tetraacetate on acetylation, however, is still unexplained.

EXPERIMENTAL

2,5-Dimethoxyquinone and acetyl chloride

To a mixture of 2,5-dimethoxyquinone (5 g) and acetyl chloride (50 ml), concentrated sulfuric acid (5 ml) was added in portions. The quinone slowly dissolved. After three hours the brown-colored solution was poured into ice water (1500 ml) containing sodium hydrogen carbonate (50 g). An oil precipitated, which soon solidified to a crystalline mass. The crystals were collected and recrystallized from ethanol. Three recrystallizations yielded 5.2 g of a pure substance melting at 90–91°. The substance is a dimethoxydichlorophenol acetate, previously prepared by Oliverio in an analogous reaction with aluminium chloride as catalyst³. Oliverio reports the melting point as 92°.

$C_{10}H_{10}O_4Cl_2$ (265.1)	Calc.	OCH_3	23.6
	Found	»	23.5

The mother liquors contained another substance, which could not be obtained in a pure state by recrystallization. When the mother liquors were hydrolyzed with sodium hydroxide in ethanol, and the ethanolic solution diluted with water, this substance could be obtained in an almost pure state by steam distillation or ether extraction of the alkaline solution. The substance was recrystallized from light petroleum. M. p. 89–90°, alone, or on admixture with a specimen of trichloroquinol dimethyl ether, prepared from trichloroquinol by methylation with diazomethane.

$C_8H_7O_2Cl_3$ (241.5)	Calc.	OCH ₃	25.7
	Found	»	25.5

2,5-Dimethoxyquinone and acetyl bromide

Acetyl bromide (40 ml) was added to 2,5-dimethoxyquinone (5 g). After a few minutes the quinone was dissolved. The solution had the dark red color of bromine. The solution was poured into ice water (500 ml) in which sodium acetate (40 g) had been dissolved. An oil separated which soon solidified, and was recrystallized from ethanol. Yield 6.3 g. The substance melted at 182–183°, alone, or on admixture with 2,5-dimethoxyquinol diacetate, prepared in a good yield by treating 2,5-dimethoxyquinone with zinc dust and acetic anhydride.

$C_{12}H_{14}O_6$ (254.2)	Calc.	OCH ₃	24.4
	Found	»	24.0

2,6-Dimethoxyquinone and acetyl bromide

Acetyl bromide (40 ml) was slowly added to 2,6-dimethoxyquinone (10 g). A small amount of mercuric bromide (0.1 g) accelerated the reaction but was not necessary. With mercuric bromide as catalyst the reaction was vigorous, and the reaction mixture had to be cooled with ice water. After a few minutes the reaction was complete and the yellow solution was poured into ice water (1 000 ml) and sodium hydrogen carbonate (30 g) added. A yellow oil separated and solidified after about an hour to a crystalline mass (16 g). This proved to be mixture of three substances. The chief product could be obtained in a pure state by four recrystallizations from ethanol. It melted at 108–109°, alone, or on admixture with 2,6-dimethoxybromoquinol diacetate, prepared from 2,6-dimethoxybromoquinone by reductive acetylation with zinc dust and acetic anhydride.

$C_{12}H_{13}O_6Br$ (333.1)	Calc.	OCH ₃	18.6	Br	24.0
	Found	»	18.7	»	23.8

This substance, when hydrolyzed with sulfuric acid in methanol, decomposed into 2,6-dimethoxyquinone and hydrogen bromide. The mother liquors were treated with sulfuric acid in methanol, the separated quinone was removed by filtration, the solution concentrated and acetylated. By these operations the monobromo diacetate was eliminated from the mixture. The residue was fractionated by recrystallizations from methanol. Two pure substances, melting at 126–127° and 103–105° respectively were obtained. They proved to be identical with the previously known diacetates of 2,6-dimethoxyquinol and 3,5-dibromo-2,6-dimethoxyquinol respectively. We prepared those substances by reductive acetylation of the 2,6-dimethoxyquinone and its dibromo derivative.

2,6-Dimethoxymonobromoquinol

In an attempt to prepare 2,6-dimethoxymonobromoquinol, 2,6-dimethoxymonobromoquinol diacetate (2.0 g) was dissolved in methanol with 1 % sulfuric acid (5 ml) and refluxed for 15 minutes. A yellow, crystalline substance precipitated, which was collected and recrystallized from acetic acid. Yield 0.7 g. M. p. 248–249°. The melting point was not depressed on admixture with 2,6-dimethoxyquinone.

A small amount of 2,6-dimethoxymonobromoquinone was reduced with zinc dust in boiling acetic acid. The colorless solution was diluted with water and extracted with ether. The ether solution was washed with sodium hydrogen carbonate solution and water, and dried over anhydrous sodium sulfate. When this still colorless solution was concentrated, even under reduced pressure, the substance decomposed and 2,6-dimethoxyquinone was formed. The liberated acid seemed to accelerate this decomposition. The presence of the bromoquinol, which could not be isolated, was demonstrated by the following experiment. A small amount of the bromoquinone was reduced as above. To the colorless acetic acid solution, acetic anhydride and pyridine were added and the solution refluxed for some minutes. When the mixture was poured into water, a colorless substance of m. p. 108–109°, identical with the bromoquinol diacetate described above, separated.

SUMMARY

Monobromo-2,6-dimethoxyquinol, in contradiction to other halogenoquinols, is a very unstable substance, which easily decomposes into 2,6-dimethoxyquinone and hydrogen bromide.

Trichloroquinol dimethyl ether has been isolated from the reaction mixture obtained when 2,5-dimethoxyquinone was treated with acetyl chloride and sulfuric acid.

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