

Studies on Quinones and Hydroquinones

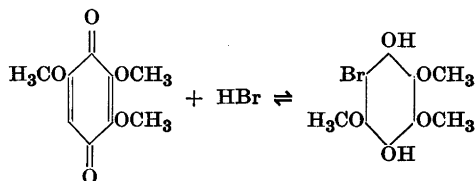
III. * Bromotrimethoxyhydroquinone

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It is well known that hydrogen chloride and bromide react with most quinones to form halogenohydroquinones, although some derivatives, such as 2,5- and 2,6-dimethoxyquinone, do not exhibit any reactivity towards these reagents. In Parts I¹ and II of this series the occurrence of the reverse type of reaction to this addition process was demonstrated with 2-chloro- and 2-bromo-3,5-dimethoxyhydroquinone, these compounds decomposing readily into 2,6-dimethoxyquinone and the corresponding hydrogen halides. The isomeric 2-chloro- and 2-bromo-3,6-dimethoxyhydroquinone were, however, quite stable substances.

The investigation has now been extended to trimethoxyquinone derivatives. Trimethoxyquinone in chloroform was found to add on hydrogen bromide with the formation of a labile substance, which easily decomposed into the starting materials. The decomposition is catalyzed by acids, but in alkali the substance seems to be rather stable. A diacetate was obtained by acetylation with acetic anhydride either in alkaline solution or in pyridine. The diacetate was identical with bromotrimethoxyhydroquinone diacetate, prepared by bromination of the trimethoxyquinone and subsequent reductive acetylation. The labile substance could be obtained by reduction of the bromoquinone by zinc dust in acetic acid. All these facts indicate that it should be bromotrimethoxyhydroquinone, and the reaction

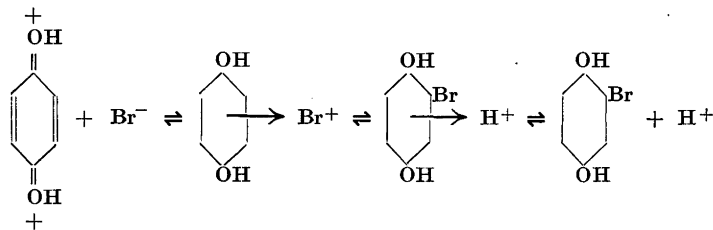
* Part II. *Acta Chem. Scand.* 6 (1952) 1048.

would appear to be the first known example of the reversible addition of a hydrogen halide to a quinone with the formation of a hydroquinone. A similar reaction, the reversible addition of hydrogen chloride to 4,4'-dimethoxydiquinone, was observed by Erdtman², but in this case the reaction product was decomposed by alkali, and an investigation by the present author³ has proved that the substance is not a hydroquinone.

The action of sodium borohydride on the quinones concerned in this investigation and some other quinones was examined. It proved to be very effective, methanolic solutions of the quinones being decolorized instantaneously. However, the method does not seem to offer any advantages over the classical methods for the reduction of simple quinones. Humic acids, both natural and artificial, are also reduced by sodium borohydride, and in this field the reagent might be useful, especially if the reduction can be developed into an analytical method, as has been done for carbohydrates⁴.

DISCUSSION

According to Dewar⁵, the addition reactions of quinones proceed through π -complexes:



In the example given by Dewar the neutral quinone molecule reacts with the anion, but as these reactions occur in an extremely acid medium, the present author prefers to write the reaction as above.

This scheme also gives a reasonable mechanism for the reverse reaction, which should be catalyzed by hydrogen ions. Electron repelling substituents decrease the redox potential of quinones, so it is natural that quinones with such substituents should show decreased additive reactivity and also that labile substances might be found among the corresponding halogenohydroquinones. It is, however, difficult to interpret the great differences in reactivity between rather similar substances, *e.g.* why 2-bromo-3,6-dimethoxyhydroquinone should be stable but not the isomeric 3,5-dimethoxyderivative. It is possible that an investigation of the redox potentials and other physical-chemical properties of these substances would contribute to a better understanding of these reactions.

EXPERIMENTAL

All melting points uncorrected. Trimethoxyquinone was prepared by the method of Huisman ⁶.

Trimethoxyhydroquinone diacetate. Reductive acetylation of trimethoxyquinone with zinc dust and acetic anhydride gave an almost quantitative yield of trimethoxyhydroquinone diacetate. Two recrystallizations from methanol yielded the pure substance, m.p. 76.5–77°. (Found: OCH_3 32.6; Calc. for $\text{C}_{13}\text{H}_{16}\text{O}_7$ (784.3): OCH_3 32.8.)

Bromotrimethoxyquinone. A solution of trimethoxyquinone (3 g) and bromine (3 g) in absolute chloroform was refluxed for 15 minutes and then evaporated to dryness under reduced pressure. The crystalline residue was recrystallized from benzene, when unchanged starting material (0.3 g) was obtained. The mother liquors were concentrated and the residue recrystallized from methanol. Repeated recrystallizations yielded almost pure bromotrimethoxyquinone (1.5 g) as red needles, m.p. 89.5–91°. (Found: OCH_3 34.3; Br. 28.0; Calc. for $\text{C}_9\text{H}_9\text{O}_5\text{Br}$ (277.1): OCH_3 33.6; Br. 28.8.)

Bromotrimethoxyhydroquinone diacetate. a) Reductive acetylation of bromotrimethoxyquinone (0.5 g) with zinc dust in acetic anhydride yielded the bromotrimethoxyhydroquinone diacetate. The substance was recrystallized twice from methanol. Yield 0.6 g, m.p. 97–98° (Found: OCH_3 25.7; Br. 21.3; Calc. for $\text{C}_{13}\text{H}_{15}\text{O}_7\text{Br}$ (363.2): OCH_3 25.6; Br. 22.0.)

b) Hydrogen bromide was passed into a solution of trimethoxyquinone (0.5 g) in chloroform (15 ml). The red colour of the solution rapidly changed to light yellow. Dry air was then bubbled through the solution to remove excess of hydrogen bromide, a small amount of calcium carbonate was added and the solution evaporated to dryness under reduced pressure at room temperature. The yellow residue was acetylated with acetic anhydride (5 ml) and pyridine (1 ml) and poured into water. An oil separated, which soon crystallized. Recrystallization from methanol yielded colourless crystals (0.65 g, 70 %), m.p. 97–98° alone or in admixture with the bromotrimethoxyhydroquinone diacetate described under a). The same acetate was obtained in a yield of 30 % when the yellow residue was dissolved in alkali and acetylated with acetic anhydride.

Decomposition of bromotrimethoxyhydroquinone. Bromotrimethoxyhydroquinone was obtained, as a yellow oil which showed tendency to crystallize either by addition of hydrogen bromide to trimethoxyquinone as described above or by reduction of bromotrimethoxyquinone with zinc dust in acetic acid. The identity of the substance was demonstrated by converting it into the diacetate. When the oil was dissolved in benzene and the solution heated, the yellow colour changed to red. On addition of a drop of conc. hydrochloric acid, the change of colour became very rapid and trimethoxyquinone, identical with authentic material, separated.

SUMMARY

Trimethoxyquinone reacts with hydrogen bromide to form bromotrimethoxyhydroquinone. In contradistinction to other reactions of the same type, this reaction is reversible.

The author wishes to thank *Statens Naturvetenskapliga Forskningsråd* for financial support and Mr. J. Paju for skilful assistance.

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Received November 18, 1952.