

Studies on Quinones and Hydroquinones

II.* Monohalogen Derivatives of 2,5- and 2,6-Dimethoxyhydroquinone

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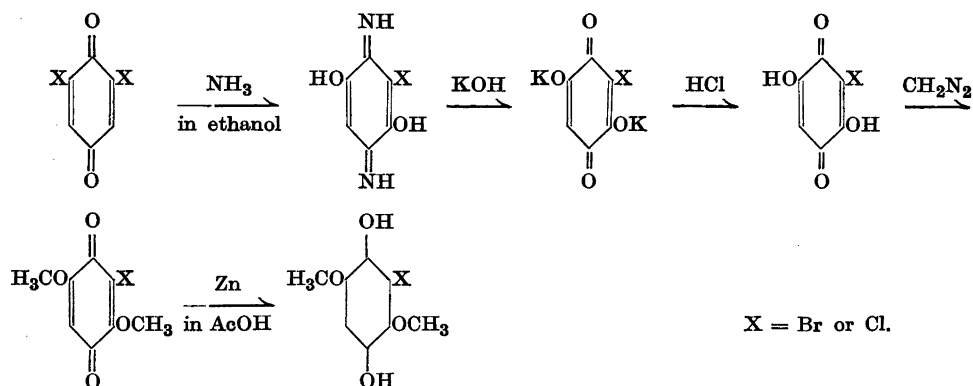
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In a previous communication¹ it was reported that 3-bromo-2,6-dimethoxyhydroquinone, obtained by hydrolysis of its diacetate or by reduction of the corresponding quinone, is a very labile substance. It decomposed so easily into 2,6-dimethoxyquinone and hydrogen bromide, that it could not be obtained in the solid state (but only in solution). The decomposition was catalyzed by acids. This seems to be the first example of the reaction which is the reverse of the wellknown addition of hydrogen halides to quinones. In the present paper the synthesis and properties of some monohalogen dimethoxyhydroquinones is reported.

Reduction of 3-chloro 2,6-dimethoxyquinone with zinc in acetic acid gave the 3-chloro 2,6-dimethoxyhydroquinone which could be acetylated to the diacetate, identical with that obtained by reductive acetylation of the quinone, and could be oxidized to the quinone with ferric chloride. Thus, it is a fairly stable substance, but when dissolved in dilute hydrochloric acid it decomposed slowly in the cold, but very rapidly on warming, 2,6-dimethoxyquinone being precipitated. 3-Chloro 2,6-dimethoxyhydroquinone, therefore, provides a second example of a halogenated hydroquinone which decomposes into the hydrogen halide and the quinone.

The corresponding chloro and bromo derivatives with the methoxyl groups in the 2 and 5 positions were prepared by the series of reactions given in the scheme below.

* Part I. On the Reactivity of 2,5- and 2,6-Dimethoxyquinone. Ref. 1.



The quinone, hydroquinone and hydroquinone diacetate could be interconverted by appropriate reactions, and the chloro and bromo hydroquinones were quite stable, even in boiling 2 *N* hydrochloric acid.

3-Bromo 2,6-dimethoxyquinone and the corresponding 2,5-derivative easily add hydrogen bromide and form the dibromo dimethoxyhydroquinones, as may have been anticipated, bearing in mind the observation of Aulin and Erdtman², that dibromo 2,6-dimethoxyhydroquinone was formed in good yield when 2,6-dimethoxyquinone was treated with one mole of bromine in chloroform at room temperature. The two monobromo quinones are, however, recovered unchanged upon attempted Thiele acetylation.

The reason for the instability of the 3-chloro and 3-bromo 2,6-dimethoxyhydroquinones is at present obscure. The fact that the dihalogenated 2,6-dimethoxyhydroquinones and the monohalogenated 2,5-dimethoxyhydroquinones are quite stable makes it probable that a very special effect is operating in the labile compounds. The search for further labile halogenated hydroquinones is being continued in order to find a reasonable explanation of the unexpected behaviour of these substances.

EXPERIMENTAL

3-Chloro-2,6-dimethoxyhydroquinone. 3-Chloro 2,6-dimethoxyquinone (0.5 g) was reduced with zinc dust in boiling acetic acid (10 ml). The solution was poured into water and extracted with ether and the extract was washed with sodium hydrogen carbonate solution, dried over calcium chloride and concentrated under reduced pressure. The residual brown oil was dissolved in hot benzene and on cooling colourless crystals (0.4) of the hydroquinone separated. Further recrystallizations from benzene yielded the pure substance, m.p. 98–99°*.

$C_8H_9O_4Cl$ (204.6) Calc. OCH_3 30.3 Found OCH_3 30.0

* All melting points uncorrected.

A small amount of the hydroquinone was dissolved in water and treated with ferric chloride. The yellow substance which precipitated was collected and recrystallized from ethanol. It melted at 146–147° either alone or in admixture with an authentic specimen of 3-chloro 2,6-dimethoxyquinone.

A small amount of 3-chloro 2,6-dimethoxyhydroquinone was dissolved in N hydrochloric acid. On warming a yellow, crystalline substance precipitated. This was collected, and recrystallized from acetic acid and then had m.p. 248–249°, undepressed on admixture with authentic 2,6-dimethoxyquinone.

3-Chloro 2,6-dimethoxyhydroquinone diacetate. The diacetate of 3-chloro 2,6-dimethoxyhydroquinone was prepared in good yield either by acetylation of the hydroquinone with acetic anhydride and pyridine or by reductive acetylation of the quinone with zinc dust and acetic acid. It was recrystallized from ethanol and melted at 111–112°.

$C_{12}H_{13}O_6 Cl$ (288.7) Calc. OCH_3 21.5 Found OCH_3 21.6

3-Bromo-2,5-dihydroxyquinone diimide. Concentrated ethanolic ammonia (50 ml) was added slowly to a solution of 2,6-dibromoquinone (20 g) in ethanol (100 ml) at 60°, and the mixture was set aside at 0° overnight. The brown imide (6.5 g) was filtered off and recrystallized from acetic acid, forming brown crystals with a metallic lustre, which decomposed without melting at about 360°.

$C_6H_5O_2N_2Br$ (217.0) Calc. N 12.9 Found N 12.6

3-Bromo-2,6-dihydroxyquinone. The above imide (4 g) was dissolved in 20 % potassium hydroxide solution (25 ml) and the mixture was heated nearly to boiling. On cooling the potassium salt of the hydroxyquinone precipitated as dark red crystals, which were collected by filtration and dissolved in water. The aqueous solution was acidified with hydrochloric acid and extracted with ether, and the ether solution was dried over calcium chloride and concentrated. The residue recrystallized from acetic acid, yielding the 3-bromo-2,5-dihydroxyquinone as brick-red crystals (1.6 g), m.p. 190° (decomp.).

$C_6H_3O_4Br$ (219.0) Calc. Br 36.5 Found Br 36.8

3-Bromo-2,5-dimethoxyhydroquinone. This substance was prepared in 80 % yield in the same way as the monochloro 2,6-dimethoxyhydroquinone. It was recrystallized from benzene-ligroin (1 : 1) and melted at 95–96°.

$C_8H_9O_4Br$ (249.1) Calc. OCH_3 24.9 Found OCH_3 24.9

The substance could be oxidized to the quinone with ferric chloride, as described for the 3-chloro-2,6-dimethoxyhydroquinone.

5-Bromo-2,5-dimethoxyhydroquinone diacetate. This substance was prepared by reductive acetylation of the quinone with acetyl bromide, with the elimination of bromine. It was also prepared from the hydroquinone by acetylation. When the substance was prepared by reductive acetylation, with zinc dust and acetic anhydride, 2,5-dimethoxyhydroquinone diacetate, m.p. 181–182°, was formed simultaneously in about 25 % yield. This side reaction did not occur when the quinone was first reduced in acetic acid solution, and then acetylated. The 3-bromo 2,5-dimethoxyhydroquinone diacetate was recrystallized from 70 % methanol and melted at 77–78°.

$C_{12}H_{13}O_6 Br$ (333.1) Calc. OCH_3 18.6 Found OCH_3 18.4

3-Chloro-2,5-dimethoxyquinone. 3-Chloro-2,5-dihydroxyquinone (4 g) was methylated with diazomethane as described above for the bromoderivative. The orange-red substance (3.6 g) was recrystallized from ethanol and melted at 123–124°.

$C_8H_7O_4 Cl$ (202.6) Calc. OCH_3 30.6 Found OCH_3 30.2

3-Chloro-2,5-dimethoxyhydroquinone. This substance, prepared in 90 % yield, in the same way as the other hydroquinones, was recrystallized from benzene-ligroin (1 : 1) and melted at 95–96°.

$C_9H_9O_4Cl$ (204.6) Calc. OCH_3 30.3 Found OCH_3 30.4

3-Chloro-2,5-dimethoxyhydroquinone diacetate. This substance, prepared from the hydroquinone by acetylation, or from the quinone by reductive acetylation with zinc and acetic anhydride, was recrystallized from 70 % methanol and melted at 70–71°.

$C_{12}H_{13}O_6Cl$ (288.7) Calc. OCH_3 21.5 Found OCH_3 21.6

SUMMARY

The 3-chloro and 3-bromo-2,5- and 2,6-dimethoxyhydroquinones, their acetates and the corresponding quinones have been prepared. Of the hydroquinones, the 2,6-dimethoxy derivatives decompose by an acid-catalyzed reaction into 2,6-dimethoxyquinone and the hydrogen halide, while the 2,5-dimethoxy derivatives and the dihalogen derivatives from both series are quite stable.

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