Halogenation of N-Substituted para-Quinone Monoimine and para-Quinone Monooxime Esters: VI.* Regular Trends in Chlorination and Bromination of N-Arylsulfonyl-1,4-benzoquinone Monoimines Alkyl-Substituted in the Quinoid Ring

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Received November 23, 2004

Abstract—Reactions of halogens with N-arylsulfonyl-1,4-benzoquinone monoimines occur with the formation of a halogenonium ion that either transforms into a carboxonium where the first halogen atom adds to the carbon in the ortho-position relative to the carbonyl carbon, or the halogenonium ion adds directly the second halogen atom.

DOI: 10.1134/S107042800605006X

This research continues the investigation of the halogenation processes of N-arylsulfonyl-1,4-benzoquinone monoimines alkyl-substituted in the quinoid ring. In the preceding publications of this series [1–3] the features of the halogenation of various N-aryl(arylsulfonyl)oximino-2,5-cyclohexadien-1-ones and N-arylsulfonyl-1,4-benzoquinone monoimines were considered, the main reaction paths and regularities were revealed.

As the last object for the study in this series we selected N-arylsulfonyl-2,3-dimethyl-1,4-benzoquinone monoimines Ia and Ib in order to establish finally the halogenation mechanism of N-arylsulfonyl-1,4-benzoquinone monoimines. Similarly to N-arylsulfonyl-3-methyl-1,4-benzoquinone monoimines [3] quinone imines Ia and Ib exist in solution in the form of a single isomer but to the anti-bond C=C of the quinoid ring in these compounds one more substituent, Me group, is attached, even more increasing the steric hindrance to the halogen addition across this bond. Therefore the halogen addition should occur strictly regiospecifically at the C=C bond of the quinoid ring lacking substituents.

The halogenation of quinone imines Ia and Ib was performed in various solvents (CHCl₃, CH₃CO₂H, CH₃CO₂H-DMF mixture, 5:1), and at different ratios quinone imine I—halogen. Depending on the experimental conditions the halogenation of quinone imines Ia and Ib gave rise mainly to stable 4-arylsulfonylimino-5,6-dihalo-2,3-dimethyl-2-cyclohexen-1-ones IIa, IIb, IIIa, and IIIb, and only at the bromination in CHCl₃ N-phenylsulfonyl-4-amino-6-bromo-2,3-dimethylphenol (IV) was isolated (Scheme 1).

The chlorination of 4-arylsulfonylamido-2,3-dimethylphenols Va and Vb depending on the experimental

![Scheme 1](image-url)

* For communication V, see [1].
conditions afforded 4-arylsulfonylimino-2,3-dimethyl-5,6-dichloro-2-cyclohexen-1-ones IIa and IIb, 4-phenylsulfonylamido-2,3-dimethyl-6-chlorophenol (VI), and 4-arylsulfonylimino-5,6-dimethyl-2,5,6-trichloro-2-cyclohexen-1-ones VIIa and VIIb (Scheme 2).

Aminophenol VI was obtained only in chloroform at the ratio substrate Va–chlorine 1:1. In this case the electrophilic substitution is likely to occur (the chlorine enters into the meta-position with respect to the most electron-withdrawing group). Then under the action of the second chlorine molecule aminophenol VI is oxidized to give quinone imine VIII, and the next chlorine molecule adds to form a compound of cyclohexene structure VIIa. The latter stage was proved by an independent synthesis, the chlorination of quinone imine VIII. Compound VIII was obtained by oxidation of aminophenol VI with lead tetraacetate. In the same way was synthesized quinone imine IX.

In CH₃CO₂H and the mixture DMF–CH₃CO₂H, 1:5, the aminophenols Va and Vb are oxidized with chlorine to the corresponding quinone imines, add a single chlorine molecule forming compounds of cyclohexene structure IIa and IIb (which were isolated at the ratios initial substance–chlorine 1:1, 1:2), eliminate an HCl molecule, and add the second molecule of Cl₂ furnishing compounds VIIa and VIIb. This scheme is supported by the fact, that the reduced form VI is not isolated in the reactions carried out in CH₃CO₂H and the mixture DMF–CH₃CO₂H, 1:5.

The bromination of aminophenols Va and Vb in CHCl₃ or CH₃CO₂H yielded only aminophenol IV, in the mixture DMF–CH₃CO₂H, 1:5, at the ratio initial compound–bromine 1:1 formed aminophenol VI; and at the ratio 1:5 compounds of cyclohexene structure IIIa and IIIb were obtained. The structure of aminophenols IV and VI was confirmed by the ¹H NMR spectra recorded after oxidation of the aminophenols to the corresponding quinone imines VIII and IX for the ¹H NMR spectra of the latter were more informative. The signal from the H⁵ atom of quinone imines VIII and IX is observed in the spectra as a singlet in a downfield region characteristic of hydrogen atoms in the ortho-position with respect to the imine carbon.

The structure of aminophenols IV and VI was confirmed by their independent synthesis by hydrohalogenation of quinone imines I. The compounds obtained were identical to aminophenols IV and VI prepared by the halogenation.

In order to prove the last stages of the chlorination and to obtain products with a higher extent of the bromination we performed the halogenation of aminophenols IV and VI, and quinone imines VIII and IX (Scheme 3). We succeeded to obtain by bromination of aminophenol IV a compound of cyclohexene structure X which we failed to isolated at the bromination of aminophenol Va.

The halogenation of quinone imines VIII and IX provided mixtures of compounds VIIa, XI and X, XII respectively. Thus the halogen molecule added both at

Ar = Ph (a), 4-MeC₆H₄ (b); Hlg = Cl (VI, VIII), Br (IV, IX).