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

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Abstract—The direction of halogen addition to N-arylsulfonyl-1,4-benzoquinone monoimines dialkyl-substituted in the quinoid ring is governed by the steric factors: the size and position of the substituent, the halogen volume, and the position of the substituent at the nitrogen. The first stage of halogenation of N-arylsulfonyl-4-aminophenols with two alkyl substituents in the phenylsulfonyl ring largely occurs as electrophilic substitution.

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In [1] was reported on the halogenation of the N-arylsulfonyl-2(3)-methyl(2-chloro)-1,4-benzoquinone monoimines, and the principal factors were established influencing the direction of the halogen addition.

The goal of the present study was the elucidation of the extent to which the steric factor influenced the halogenation direction in the case of para-quinone monoimines with two alkyl substituents in the quinoid ring (varying of the size of the substituent in the quinoid ring and its position). The results should be compared with those obtained on the corresponding para-quinone monooximes esters. To this end the halogenation was carried out using N-arylsulfonyl monoimines with various substituents (i-Pr, Me) in positions 2 and 5 of the quinoid ring of the para-quinone imines, with different positions of two methyl groups (2, 5; 2, 6, and 3, 5); the halogens employed had various atomic radii (Cl, Br).

The chlorination of quinone imines Ia–Ic–IIIa–IIIc was performed with gaseous chlorine, the bromination, with molecular bromine in various solvents (CHCl₃, AcOH, DMF–AcOH, 1 : 5) at different ratios of the initial substance and the halogen. Owing to the presence of a Me (i-Pr) group in the ortho-position with respect to the imine carbon atom these compounds exist as a single isomer.

In the halogenation of N-arylsulfonyl-2,5-dimethyl-1,4-benzoquinone imines Ia–Ic the direction of the halogen addition is governed mainly by the bulk of the halogen atom proper. The chlorination of quinone imines Ia–Ic occurred under more stringent conditions than with N-arylsulfonyl-2(3)-methyl-1,4-benzoquinone imines [1], at prolonged heating. The chlorine molecule in this instance added to the C=C bond having a substituent in the ortho-position with respect to the carbonyl carbon, namely to the syn-bond. It was already stated in [2, 3] that in the halogenation of para-quinone oximes esters the C=C bond in the syn-position to the substituent at the nitrogen atom was more reactive. Accordingly the chlorination of quinone imines Ia–Ic resulted in cyclohexene (hemiquinoid) structures: 4-arylsulfonylimino-3,6-dimethyl-5,6-dichloro-2-cyclohexen-1-ones IVa–IVc (Scheme 1).

* For communication IV, see [1].

Scheme 1.

Ar = Ph (a), 4-MeC₆H₄ (b), 3-NO₂C₆H₄ (c).
The bromination proceeded easier, at slight short heating. The bulkier bromine molecule added to the anti-bond C=C with a substituent in the ortho-position with respect to the imine carbon atom, consequently, to the more spatially accessible C=C bond of the quinoid ring, affording 4-aryl-sulfonylimino-2,5-dimethyl-5,6-dibromo-2-cyclohexen-1-ones Va–Ve (Scheme 1) (in quinone imine I the syn-bond C=C of the quinoid ring contained a Me group and suffered a sterically hindrance from the ArSO2 group).

In the halogenation of 2,5-dimethyl-substituted para-quinone monoacetimates esters [4] the products obtained resulted from halogen addition to each of the C=C bonds of the quinoid ring, therefore the chlorine and bromine molecules could add both to the C2=C3 and C5=C6 bonds of the quinoid ring. The chlorination of 2,5-dimethyl-substituted quinone imines Ia–Ic affords only the products of addition to the C2=C3 bond, and the bromination, to the C5=C6 bond; it means that the addition direction is governed by the size of the halogen atom. The calculations by PM3 method demonstrated that in quinone imine Ia the difference in polarization of the C2=C3 and C5=C6 bonds (see the table) was less pronounced than in the corresponding 2,5-dimethyl-1,4-quinone monoacetimine ester [2]. Therefore the chlorine molecule adds across the less polarized and more active C2=C3 bond, and the bulkier bromine molecule, across the more sterically accessible C5=C6 bond; thus the steric factor is relatively more important for the regioselectivity of the halogen addition to quinone imines than to the corresponding para-quinone oximes esters, as is proved experimentally.

At the chlorination of N-arylsulfonyl-6-isopropyl-3-methyl-1,4-benzoquinone imines IIa–IIc the molecule of Cl2 added to either of C=C bonds of the quinoid ring. This may be due to the presence of a bulkier substituent, i-Pr, at the C=C bond in the syn-position to the substituent at the nitrogen, and therefore addition to the C5=C6 bond is impeded. The addition of the bromine molecule as expected by analogy to quinone imines Ia–Ic occurred only at the more accessible C=C containing a Me substituent (Scheme 2).

The calculations by PM3 method showed that same as in 2,5-dimethyl-substituted quinone imine Ia in quinone imine IIa difference in the polarization of the bonds C2=C3 and C5=C6 (see the table) is less pronounced than in the corresponding para-quinone oxime ester [2]. Hence as in para-quinone imines Ia–Ic the steric factor governs the direction of the halogen addition.

The chlorination of N-arylsulfonyl-2-methyl-5-isopropyl-1,4-benzoquinone monoacetimates IIIa–IIIc occurred exclusively across the C2=C3 bond of the quinoid ring containing a Me group. At the bromination both products of Br2 addition to either C=C bond of the quinoid ring were obtained. This fact is due to the presence in quinone imines IIIa and IIIb of the bulky isopropyl group at the C5=C6 bond in the anti-position with respect to ArSO2 substituent. This bond, more sterically accessible in quinone imines Ia–Ic and IIa–Iic, is difficultly accessible for bulky bromine molecule in compounds III (Scheme 3). The PM3 calculations show that the difference in the polarization of the C=C bonds of the quinoid ring in quinone imine IIIa is comparable with the

<table>
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<th>Compd. no.</th>
<th>qC2</th>
<th>qC3</th>
<th>Δq1</th>
<th>qC4</th>
<th>qC5</th>
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</tbody>
</table>

*Δq1 = |qC2 – qC3|; **Δq2 = |qC4 – qC5|; **Δq = Δq1 – Δq2.