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Chlorination of *N*-(*N*-Arylsulfonylarylimidoyl)-1,4-benzoquinone Imines and Their Reduced Forms

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Abstract—The study of chlorination of *N*-(*N*-arylsulfonylarylimidoyl)-1,4-benzoquinone imines and of *N*-(*N*-arylsulfonylarylimidoyl)-1,4-aminophenols revealed that the dominant stage in the process was the formation of cyclohexene structures, 4-(*N*-arylsulfonylarylimidoyl)imino-2,5,6-trichloro-2-cyclohexene-1-ones, resulting from addition of a Cl_2 molecule across the C=C bond of the quinoid ring. These substances suffer a prototropic rearrangements yielding *N*-(*N*-arylsulfonylarylimidoyl)-2,3,6-trichloro-4-aminophenols. The latter are the most common reaction products. The products of deeper chlorination were also obtained.

In the preceding investigation on chlorination of *N*-arylsulfonyl-1,4-benzoquinone imines and *N*-arylsulfonyl-1,4-aminophenols we demonstrated that depending on the solvent, temperature, and molar ratio of the initial substrate to chlorine the reaction gave rise to *N*-arylsulfonyl-2,3,6-trichloro-4-aminophenols, *N*-arylsulfonyl-2,3,6-trichloro-1,4-benzoquinone imines, and *N*-arylsulfonyl-2,3,5,6-tetrachloro-1,4-benzoquinone imines [1]. We failed to isolate products containing one or two chlorine atoms. We also obtained semiquinoid structures resulting from addition of a Cl_2 molecule across a double bond of the quinoid ring, 2,3,5,6,6-pentachloro[2]- and 2,3,5,5,6,6-hexachloro[1]-4-arylsulfonylimino-2-cyclohexen-1-ones.

Several schemes of multistage chlorination process were suggested [1]. (1) *N*-Arylsulfonyl-4-aminophenols first are oxidized with Cl_2 to the respective quinone imines that further can add a Cl_2 molecule followed by dehydrochlorination or add HCl molecule with subsequent oxidation. The above chlorination products arise due to alternation of these processes. (2) N-Arylsulfonyl-1,4-benzoquinone imines first add a chlorine molecule to the C=C bond of the quinoid ring followed by dehydrochlorination, and the arising *N*-arylsulfonyl-2-chloro-1,4-benzoquinone imine can either add a chlorine molecule attended by dehydrochlorination or take up HCl molecule with subsequent oxidation.

The reason why not a single chlorination experiment with *N*-arylsulfonyl-1,4-benzoquinone imines or their reduced forms yielded chlorination products containing one or two chlorine atoms remained unclarified.

The chlorination of *N*-aroyl-4-aminophenols afforded only *N*-aroyl-2,3,6-trichloro-4-aminophenols and *N*-aroyl-2,3,5,6-tetrachloro-1,4-benzoquinone imines [3]. The stability of *N*-aroyl-1,4-benzoquinone imines unsubstituted in the ring is very low, and therefore their reactivity, in particular in chlorination, was not investigated.

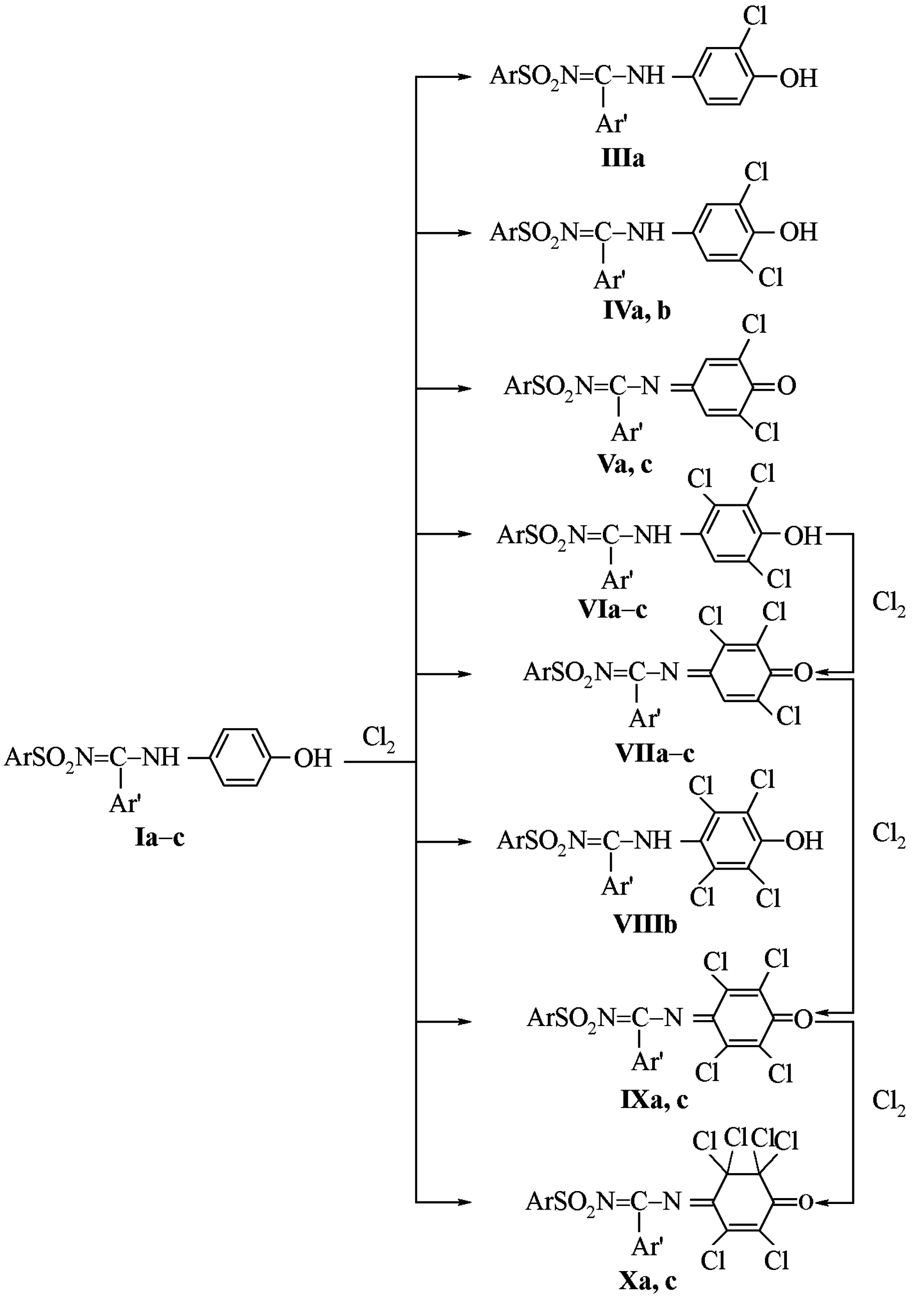
N-(*N*-Arylsulfonylarylimidoyl)-1,4-benzoquinone imines are derivatives of N-aroyl-1,4-benzoquinone imines where in the aroyl group the oxygen in C=O is replaced by arylsulfonylimino group ($ArSO_2N=$). Therefore we expected to obtain similar results of chlorination.

The target of this study was to investigate the chlorination process of *N*-(*N*-arylsulfonylarylimidoyl)-1,4-benzoquinone imines and reduced forms thereof and to reveal by this example the intermediate stages of the process that provides prevailingly products containing three chlorine atoms.

The chlorination of *N*-(*N*-arylsulfonylarylimidoyl)-1,4-aminophenols (**Ia–c**) and *N*-(*N*-arylsulfonylarylimidoyl)-1,4-benzoquinone imines (**IIa, b**) was performed with a flow of chlorine gas through a solution of a substrate at a rate of 15–20 ml per min. Acetic acid, dimethylformamide, a mixture of acetic acid and DMF (5 : 1), and chloroform were used as solvents. The amount of chlorine passed through the reaction mixture was evaluated from the gained weight save at the use of chloroform as solvent.

In chlorination of *N*-(*N*-arylsulfonylarylimidoyl)-1,4-aminophenols (**Ia–c**) depending on the reaction conditions individual compounds **III–X** were isolated (Scheme 1).

Scheme 1.



Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b, c**); Ar' = C_6H_5 (**a, b**), 4-ClC_6H_4 (**c**).

In chlorination runs with aminophenols **Ia, c** in acetic acid, chloroform, and DMF at the molar ratio substrate:chlorine of 1 : 1–1 : 2 we succeeded in isolating monochloro and dichloro derivatives of aminophenol and benzoquinone imine **IIIa, IVa, Va, c**.

In the only case at chlorination of *N*-(*N*-phenylsulfonylbenzimidoyl)-1,4-benzoquinone imine (**IIa**) formed a monochloro derivative of *N*-(*N*-phenylsulfonylbenzimidoyl)-1,4-benzoquinone imine (**XIa**) (Scheme 2). Both chlorination of aminophenols **Ia–c** and benzoquinone imines **IIa, b** usually afforded *N*-(*N*-arylsulfonylarylimidoyl)-2,3,6-trichloro-4-aminophenols **VIa–c**.

At considerable excess of chlorine form also N-substituted 2,3,6-trichloro-1,4-benzoquinone imines **VIIa–c**, 2,3,5,6-tetrachloro-4-aminophenols

Melting points and elemental analyses of compounds **Xa–c, XIVa, b, XVa, b**

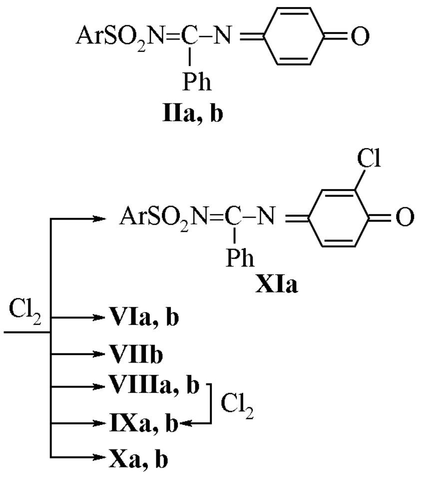
Compd. no.	mp, °C (solvent for recrystallization)	Found, %		Formula	Calculated, %	
		Cl	H		Cl	H
Xa	170 (CH_3CO_2H)	37.68, 37.91	4.97, 5.13	$C_{19}H_{10}Cl_6N_2O_3S$	38.05	5.01
Xb	165 (CH_3CO_2H)	36.69, 37.07	4.82, 4.95	$C_{20}H_{12}Cl_6N_2O_3S$	37.12	4.89
IXc	168 (CH_3CO_2H)	40.11, 40.37	4.52, 4.73	$C_{20}H_{11}Cl_7N_2O_3S$	40.85	4.61
XIVa	186 (CH_3CO_2H)	21.39, 21.41	4.21, 4.26	$C_{13}H_{11}Cl_2NO_3S$	21.34	4.22
XIVb	136 (C_6H_6)	20.39, 20.45	4.00, 4.11	$C_{14}H_{13}Cl_2NO_3S$	20.48	4.05
XVa	178 (CH_3CO_2H)	21.43, 21.49	4.24, 4.31	$C_{13}H_9Cl_2NO_3S$	21.47	4.24
XVb	149 (CH_3CO_2H)	20.55, 20.59	4.09, 4.12	$C_{14}H_{11}Cl_2NO_3S$	20.60	4.07

VIIIa, b, 2,3,5,6-tetrachloro-1,4-benzoquinone imines **IXa–c**, and 4-(*N*-arylsulfonylarylimidoylimino)-2,5,6-trichloro-2-cyclohexene-1-ones **Xa–c**; however these substances do not arise in all cases of chlorination of aminophenols **Ia–c** and benzoquinone imines **IIa, b** (cf. Schemes 1 and 2).

Thus the chlorination of *N*-(*N*-arylsulfonylarylimidoyl)-1,4-aminophenols (**Ia–c**) and 1,4-benzoquinone imines **IIa, b** affords wider range of chlorination products than has been observed with *N*-arylsulfonyl-1,4-benzoquinone imines [1] and *N*-aroyl-1,4-benzoquinone imines [3], although in the most cases *N*-(*N*-arylsulfonylarylimidoyl)-2,3,6-trichloro-4-aminophenols **VIa–c** are obtained.

Treating with chlorine in DMF solution of *N*-(*N*-arylsulfonylarylimidoyl)-2,3,6-trichloro-4-aminophenols **VIa–c** at moderate ratios chlorine:substrate afforded oxidation products of the initial compounds, *N*-(*N*-arylsulfonylarylimidoyl)-2,3,6-trichloro-1,4-benzoquinone imines **VIIa–c**. The latter on chlorination in acetic acid at heating and large chlorine excess or in DMF furnish *N*-(*N*-arylsulfonylarylimidoyl)-2,3,5,6-tetrachloro-1,4-benzoquinone imines **IXa–c** that can be converted into hexachloro semiquinoid derivatives **Xa–c** only by treating with large excess of chlorine in DMF.

Scheme 2.



Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**).

We failed to prepare compounds **VIIIa–c** by chlorination of derivatives **VIIa–c**. The formation of tetrachloroquinone imines **IXa, c** from trichloroquinone imines **VIIa, c** evidences formation of a semiquinoid structure, 4-(N-arylsulfonylarylimidoylimino)-2,3,5,6,6-pentachloro-2-cyclohexene-1-one, that is further dehydrochlorinated to yield tetrachloroquinone imines **IXa, c**.

N-(*N*-arylsulfonylarylimidoyl)-2,3,5,6-tetrachloro-4-aminophenols **VIIIa, b** are oxidized by chlorine in DMF into the corresponding quinone imines **IXa, b**.

The composition and structure of compounds **Xa–c** were proved by elemental analyses (see table), IR, ^1H and ^{13}C NMR spectra.

In the IR spectra of compounds **Xa–c** the absorption bands in the regions 1740– 1730, 1695–1690, 1590–1585, 1335–1325 and 1170–1165 cm^{-1} are present characteristic of groups C=O, C=N and SO_2 respectively. In the ^1H NMR spectra of compounds **Xa, b** the corresponding signals from Ar and Ar' groups ($CDCl_3$), δ, ppm: **IXa** 7.44–7.80 m (5H, C_6H_5–C=N), 7.52–7.06 m (5H, $C_6H_5SO_2$); **IXb** 7.43–7.80 m (5H, C_6H_5–C=N), 7.32–7.93 d.d (4H, 4-$CH_3C_6H_4SO_2$), 2.44 s (3H, CH_3) are observed.

In the ^{13}C NMR spectra of compounds **Xa, b** appear two signals in the region δ 89–90 ppm characteristic of two sp^3-hybridized carbon atoms of the semiquinoid structure; the other signals are in agreement with the assumed structure δ, ppm: Xa 172.53 (C=O), 147.14 (C=N), 140.69 (C^2), 138.25 (C^3), 90.00 (C^6), 89.11 (C^5) (cyclohexene ring); 162.25 (C=N), 134.07 (C^4), 131.24 (C^1), 129.10 (C^2, C^6), 128.81 (C^3, C^5) (C_6H_5–C=N), 138.86 (C^1), 132.95 (C^4), 128.35 (C^3, C^5), 127.21 (C^2, C^6) ($C_6H_5SO_2$); **Xb** 172.59 (C=O), 147.03 (C=N), 143.86 (C^2), 138.20 (C^3), 90.32, 89.99 (C^6), 89.44, 89.17 (C5) (cyclohexene ring), 161.99 (C=N), 133.99 (C^4), 129.44 (C^2, C^6), 129.07 (C^3, C^5) (C_6H_5–C=N), 138.92 (C^1), 137.74 (C^4), 128.37 (C^3, C^5), 127.35 (C^2, C^6), 21.55 (CH_3) (4-$CH_3C_6H_4SO_2$).

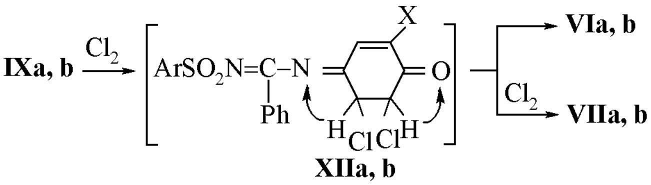
The other chlorination products according to IR spectra are identical to previously synthesized compounds [1, 4] with the known structure.

The chlorination of *N*-(*N*-arylsulfonylbenzimidoyl)-2-chloro-1,4-benzoquinone imines **XIa, b** with equimolar amount of chlorine afforded *N*-(*N*-aryl sulfonylbenzimidoyl)-2,3,6-trichloro-4-aminophenols **VIa, b** in high yield. At the double excess of chlorine formed *N*-(*N*-arylsulfonylbenzimidoyl)-2,3,6-trichloro-1,4-benzoquinone imines **VIIa, b**. The reduction of the ratio Cl_2:substrate resulted in lower yield of aminophenols **VIa, b**, in the reaction mixture remained unreacted initial quinone imine, but no compounds **IVa, b** or **Va, b** containing two chlorine atoms were formed (Scheme 3).

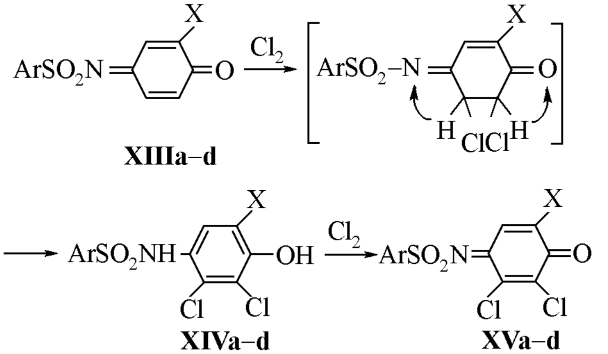
Besides in the course of quinone imines **XIa, b** chlorination into aminophenols **VIa, b** unstable intermediate compounds **XIIa, b** of light yellow color appeared that decolorized within several minutes during filtration. Compounds **XIIa, b** obviously possessed semiquinoid structure: 4-(*N*-arylsulfonylbenzimidoyl)imino-2,5,6-trichloro-2-cyclohexene-1-ones. We failed to characterize these unstable compounds in any way, even registering of IR or NMR spectra was impossible.

Thus we established that one of the dominant stages in the chlorination of *N*-(*N*-arylsulfonylarylimidoyl)-1,4-benzoquinone imines (**II**) and their reduced forms **I** is formation of semiquinoid structures by addition of a chlorine molecule across the C=C bond of the quinoid ring. These intermediate compounds further undergo prototropic rearrangement affording 2,3,6-trichloro-4-aminophenols **VI**. It is therefore understandable why the chlorination of compounds **I** and **II**, also of *N*-arylsulfonyl-1,4-benzoquinone imines, their reduced forms, and *N*-aroyl-4-aminophenols results in the corresponding 2,3,6-trichloro-4-aminophenols [1, 3]. The above reasoning shows that in the formation of the corresponding 2,3,6-trichloro-4-aminophenols neither the alternation of oxidation and hydrochlorination nor addition of Cl_2 to the C=C bond of the quinone imine followed by dehydrochlorination play the major role in the general scheme of transformations during the chlorination of *p*-quinone imines and their reduced derivatives as has been presumed in [1].

Scheme 3.



Scheme 4.



Ar = C_6H_5 (**a, d**), 4-$CH_3C_6H_4$ (**b**), 4-ClC_6H_4 (**c**); Œ= CH_3 (**a, b**), Cl (**c, d**).

We additionally supported our assumption on the dominant role in the chlorination of the N-substituted *p*-quinone imines and the reduced forms thereof of the Cl_2 addition across the C=C bond in the quinoid ring followed by prototropic rearrangement by the study of chlorination of 2-substituted *N*-arylsulfonyl-1,4-benzoquinone imines **XIIIa–d** (Scheme 4).

At equimolar ratio of chlorine to the substrate aminophenols **XIVa–d** were obtained in high yield. The increase in the ratio Cl_2:substrate to 2 : 1 resulted in formation of the corresponding *N*-arylsulfonyl-1,4-benzoquinone imines **XVa–d**, at the reduced ratio the yield of aminophenols **XIVa–d** decreased, and in the reaction mixture were found unreacted quinone imines **XIIIa–d**.

The composition and structure of compounds **XIVa, b, XVa, b** was proved by elemental analyses, IR and ^1H NMR spectra. In the IR spectra of compounds **XIVa, b** are present absorption bands in the range 3515–3480, 3260–3240, 1340–1330 and 1180–

1170 cm^{-1} characteristic of OH, NH, and SO_2 groups respectively, in the IR spectra of compounds **XVa, b** the bands in the range 1670–1660, 1585–1575, 1560–1550, 1330– 1325 and 1170–1165 cm^{-1} appear characteristic of C=O, C=C, C=N and SO_2 groups respectively. In the ^1H NMR spectra of compounds **XVa, b** appears a characteristic quartet of the H^3 proton from the quinoid ring neighboring to a CH_3 group. The other signals are in agreement with the assumed structure ($CDCl_3$), δ, ppm: **XVa** 8.04 q (1H, H^3), 2.22 d (3H, CH_3), 7.58–7.08 m (5H, $C_6H_5SO_2$); **XVb** 8.09 q (1H, H^3), 2.21 d (3H, CH_3), 7.38–7.94 d.d (4H, 4-$CH_3C_6H_4SO_2$), 2.48 s (3H, CH_3).

Compounds **XIVc, d, XVc, d** according to IR spectra are identical to the samples with the known structure described in [1, 4].

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from KBr pellets. ^1H and ^{13}C NMR spectra were registered on Varian VXR-300 instrument at operating frequencies 300 and 75.4 MHz respectively with TMS as external reference.

Reaction mixtures were analyzed by TLC on Silufol UV-254 plates. Chloroform was used as solvent, as eluents were used mixtures of alcohol–chloroform, 1:1, and benzene–hexane, 10:1, development under UV irradiation.

The initial compounds were synthesized by procedures described in [5], by acylation of *p*-aminophenol with appropriate *N*-arylsulfonylarylimidoyl chlorides in a mixture DMF–acetic acid, 1:3, followed by oxidation with lead tetraacetate in acetic acid. In reaction were brought recrystallized substances and dried solvents.

***N*-(*N*-Phenylsulfonylbenzimidoyl)-2-chloro-4-aminophenol (IIIa).** Through a solution of 0.5 g of aminophenol **Ia** in 3 ml of acetic acid was passed at 20°C a flow of chlorine gas till the gained weight corresponded to equimolar ratio substrate:chlorine. The reaction product precipitated after the end of chlorination. The product was recrystallized from acetic acid, yield 56%.

***N*-(*N*-Phenylsulfonylbenzimidoyl)-2-chloro-1,4-benzoquinone imine (XIa).** Through a solution of 0.5 g of quinone imine **IIa** in 3 ml of a mixture DMF–acetic acid, 1:5, was passed at 20°C a flow of chlorine gas till the gained weight corresponded to equimolar ratio substrate:chlorine. The reaction product precipitated after the end of chlorination. The product was recrystallized from acetic acid, yield 35%.

***N*-(*N*-Arylsulfonylarylimidoyl)-2,6-dichloro-4-aminophenols (IVa, b).** Through a solution of 0.5 g of aminophenol **Ia, b** in 3 ml of acetic acid or $CHCl_3$ was passed at 20–25°C a flow of chlorine gas till the gained weight corresponded to the desired ratio substrate:chlorine, 1:2. The reaction product **IVa, b** precipitated after the end of chlorination. The product was recrystallized from acetic acid, yield of dichloride **IVa** 63%, that of dichloride **IVb** 42%.

In $CHCl_3$ aminophenol **IVa** was prepared at 20°C. The molar ratio substrate:chlorine was not determined, and chlorine was passed till the product started to precipitate. Yield of compound **IVa** 45%.

***N*-(*N*-Arylsulfonylarylimidoyl)-2,6-dichloro-1,4-benzoquinone imines (Va, c).** To a solution of 0.5 g of aminophenol **Ia, c** in 3 ml of acetic acid or DMF was passed a flow of chlorine gas till the gain in weight corresponded to the desired ratio substrate:chlorine, 1:2. Quinone imine Va was obtained by chlorination in DMF at 40°C. The reaction product was precipitated by adding water and recrystallized from acetic acid, yield 52%. Quinone imine **Vc** was obtained by chlorination in acetic acid at 25°C. The reaction product precipitated after the end of chlorination. The product was recrystallized from acetic acid, yield 42%.

***N*-(*N*-Arylsulfonylarylimidoyl)-2,3,6-trichloro-4-aminophenols (VIa–c).** (a) Through a solution of 0.5 g of aminophenol **Ia–c** in 3 ml of acetic acid or a mixture of DMF and acetic acid, 1:5, was passed a flow of chlorine gas till the gain in weight corresponded to the desired ratio substrate:chlorine. Aminophenols **VIa–c** were prepared in the acetic acid at the molar ratio substrate:chlorine from 1:2 to 1:4 and at a temperature 20–90°C. The highest yield of product **VIa** (58%) was obtained at 30°C and molar ratio substrate:chlorine = 1:3, for product **VIb** the yield of 67% was obtained at 20°C and the molar ratio 1:4, for compound **Vc** the yield of 56% was reached in reaction performed at 90°C and molar ratio 1:4. Compound **VIa** in the mixture DMF–acetic acid, 1:5, was prepared at the following temperatures and molar ratios substrate:chlorine: 30–50°C, 1:1.5–1:2.5. The best yield (46%) was obtained at 30°C and molar ratio substrate:chlorine 1:1.5.

(b) The chlorination of quinone imines **IIa, b** was carried out similarly to the above described procedures. Aminophenols **VIa, b** were prepared in acetic acid, in a mixture DMF–acetic acid, 1:5, and in $CHCl_3$. In the acetic acid at 20°C and the molar ratio substrate: chlorine 1:2 the aminophenols were prepared in the following yields: **VIa**, 41%; **VIb**, 39%.

In the mixture DMF–acetic acid, 1 : 5, aminophenols **VIa, b** were chlorinated at 20–50°C and molar ratio substrate : chlorine from 1 : 1 to 1 : 2. The highest yields were reached at the following temperature and molar ratio: **VIa**, 20°C, 1 : 1, 83%; **VIb**, 35°C, 1 : 1, 79%. Compound **VIa** was prepared in $CHCl_3$ in the temperature range 20–35°C at molar ratio of the reagents from 1 : 1 to 1 : 5. The best yield (42%) of chloride **VIa** was obtained at 35°C and molar ratio of the reagents 1 : 5.

(c) Compounds **VIa, b** were obtained by chlorination of quinone imines **XIa, b** along procedure similar to the above described. The reaction was carried out in acetic acid at 60–70°C and molar ratio substrate : chlorine from 1 : 0.5 to 1 : 1.5. The highest yields of aminophenols **VIa, b** was obtained at molar ratio substrate : chlorine 1 : 1: for compound **VIa** 89%, for compound **VIb** 70%.

In all experiments the reaction products **VIa–c** precipitated to the end of chlorination and were recrystallized from acetic acid.

***N*-(*N*-Arylsulfonylarylimidoyl)-2,3,6-trichloro-1,4-benzoquinone imines (VIIa–c). (a) The chlorination of aminophenols Ia–c** was carried out as described above in acetic acid, DMF, and a mixture DMF–acetic acid, 1 : 5. Quinone imine **VIIa** was prepared by chlorination in CH_3COOH at 30°C and molar ratio substrate: chlorine 1 : 4. The reaction product was precipitated by water addition, yield 49%. In DMF the quinone imines **VIIa–c** were obtained at 30–45°C and the molar ratios of substrate to chlorine from 1 : 2 to 1 : 6. The reaction product precipitated after completion of the chlorination. The highest yields were obtained at the following temperatures and molar ratios of the reagents: compound **VIIa**, 30°C, 1 : 4, 73%; **VIb**, 35°C, 1 : 6, 92%; **VIIc**, 35°C, 1 : 4, 79%. In the mixture DMF–acetic acid, 1 : 5, the yields obtained at the following temperatures and molar ratios of the reagents were as follows: compound **VIIa**, 50°C, 1 : 3, 48%; compound **VIIc**, 30°C, 1 : 2, 53%. Reaction products **VIIa–c** precipitated to the end of chlorination and were recrystallized from acetic acid.

(b) The chlorination of compound **IIb** was carried out along the above described procedures. Quinone imine **VIIb** was prepared by chlorination in DMF at 30°C and molar ratio substrate : chlorine 1 : 2, from the reaction mixture the product was precipitated with water and recrystallized from acetic acid, yield 39%. The process was performed also in the mixture DMF–acetic acid, 1 : 5, at 25–30°C and the reagents ratio from 1 : 4 to 1 : 5. Product **VIIb** precipitated to the end of chlorination. The highest yield (71%) of compound **VIIb** was obtained at 30°C and the reagents ratio 1 : 5.

(c) Quinone imines **VIIa, b** were prepared by oxidation with chlorine of the corresponding amino phenols **VIa, b** along the procedures similar to the above described. The process was carried out in DMF at 20°C and the molar ratio substrate: chlorine 1 : 3 for compound **VIIa**, 1 : 1 for compound **VIIb**. The reaction products were precipitated by adding water and were recrystallized from acetic acid. Yield of compound **VIIa** 96%, of compound **VIIb** 93%.

***N*-(*N*-Arylsulfonylarylimidoyl)-2,3,5,6-tetrachloro-4-aminophenols (VIIIa, b).** (a) Aminophenol **VIIIb** was prepared from aminophenol **Ib** in a similar way as above in a mixture DMF–CH_3COOH, 1 : 5, at 35–50°C and the molar ratio of the reagents from 1 : 2 to 1 : 4. The reaction product precipitated to the end of chlorination. The highest yield (5%) of aminophenol **VIIIb** was obtained at 35°C and reagents ratio 1 : 4.

(b) Aminophenols **VIIIa, b** were synthesized from the corresponding quinone imines **IIa, b** in the similar way as described above in CH_3COOH or $CHCl_3$. In the acetic acid aminophenols **VIIIa, b** were prepared in the temperature range 25–80°C and at molar ratio substrate:chlorine from 1 : 1 to 1 : 5. The best yield was obtained at 80°C and 1 : 5 ratio (41% for compound **VIIIa** and 45% for compound **VIIIb**). In $CHCl_3$ compounds **VIIIa, b** were obtained at 40°C and reagents molar ratio 1 : 5 in 39 and 35% yield respectively. The products precipitated to the end of chlorination and were recrystallized from acetic acid.

***N*-(*N*-Arylsulfonylarylimidoyl)-2,3,5,6-tetrachloro-1,4-benzoquinone imines (IXa–c).** (a) Quinone imines **IX** were prepared from aminophenols **Ia, c** in a similar way as above in DMF or a mixture DMF–CH_3COOH, 1 : 5. Reaction in DMF occurred at 35–50°C and the molar ratio of the reagents from 1 : 4 to 1 : 6. The highest yield of chlorides was obtained at the following temperature and reagents ratio: for compound **IXa**, 35°C, 1 : 5, 66%; for compound **IXc**, 40°C, 1 : 6. 81%. In the DMF–CH_3COOH mixture, 1 : 5, compound **IXc** was prepared at 30°C and substrate:chlorine ratio 1 : 4 in 30% yield. The products precipitated to the end of chlorination and were recrystallized from acetic acid.

(b) Quinone imines **IXa, b** were prepared from the corresponding quinone imines **IIa, b** in a similar way as above in a mixture DMF–CH_3COOH, 1 : 5 at

30–80°C and the reagents ratio from 1 : 3 to 1 : 5. The products were precipitated from the reaction mixture with water and recrystallized from acetic acid. The best yield of the reaction products was obtained at temperature and molar ratio of the initial compounds: of 30°C and 1 : 4, 80° and 1 : 3 for compounds **IXa** (90%) and **IXb** (52%) respectively.

(c) Quinone imines **IXa–c** were prepared from the corresponding quinone imines **VIIa–c** in a similar way as above in DMF at 20°C and the molar reagents ratio 1 : 3. The products were precipitated from the reaction mixture with water and recrystallized from acetic acid. The yield of the products was as follows: **IXa**, 91%; **IXb**, 87%; **IXc**, 81%.

(d) Quinone imines **IXa, b** were prepared from the corresponding aminophenols **VIIIa, b** in a similar way as above in DMF at 30°C and the molar reagents ratio 1 : 8. Quinone imine **IXa** was obtained in 90% yield when the chlorination was carried out at 25°C and reagents ratio 1 : 3; quinone imine **IXb** was obtained in 98% yield. The isolation and purification of compounds **IXa, b** was performed as above.

4-(*N*-Arylsulfonylarylimidoylimino)-2,3,5,5,6,6-hexachloro-2-cyclohexene-1-ones, (Xa–c). (a) Compounds **Xa–c** were obtained by procedure similar to the above described in DMF or a mixture DMF–CH_3COOH, 1 : 5. Semiquinoid substance **Xb** was obtained in 48% yield by chlorination in DMF at 80°C and molar ratio substrate : chlorine 1 : 5. Compounds **Xa–c** were prepared in the mixture DMF–CH_3COOH, 1 : 5, in the temperature range 45–80°C and molar reagents ratio from 1 : 3.5 to 1 : 6.5. The highest yields were obtained at the following temperatures and molar ratios of the reagents: compound **Xa**, 50°C, 1 : 4, 50%; **Xb**, 60°C, 1 : 6.5, 68%; **Xc**, 50°C, 1 : 6, 67%. The products precipitated to the end of chlorination and were recrystallized from acetic acid.

(b) The chlorination of quinone imine **IIa** was performed by procedure similar to the above described in DMF at 100°C and molar ratio substrate : chlorine 1 : 5. Reaction product **Xa** was precipitated from reaction mixture with water. Yield 96%. Melting points of compounds **Xa–c** are given in the table.

(c) The chlorination of quinone imines **IXa–c** was performed by procedure similar to the above described in DMF at the following temperatures and molar ratios of the reagents: compound **Xa**, 25°C, 1 : 6, yield 67%; **Xb**, 45°C, 1 : 5, yield 50%; **Xc**, 50°C, 1 : 7, yield 67%. The chlorination products were precipitated from reaction mixture with water.

***N*-Arylsulfonyl-2-methyl(chloro)-5,6-dichloro-4-aminophenols (XIVa–d).** The synthesis was carried out by chlorination of the corresponding quinone imines **XIIIa–d** along procedures described above in CH_3COOH or a mixture DMF–acetic acid, 1 : 5, at equimolar amounts of substrate and chlorine in the temperature range 25–60°C. The reaction products were either precipitated from the reaction mixture with water, or the compound precipitated spontaneously within 24 h. The yields were as follows: compound **XIVa**, 50%; compound **XIVb**, 82%; compound **XIVc**, 74%; compound **XIVd**, 77%. The melting points and elemental analyses of aminophenols **XIVa, b** first obtained are presented in the table.

***N*-Arylsulfonyl-2-methyl(chloro)-5,6-dichloro-1,4-benzoquinone imines (XVa–d)** were obtained from the corresponding quinone imines **XIIIa–d** as above, by chlorination in acetic acid or the mixture DMF–CH_3COOH, 1 : 5, at the molar reagents ratio 1 : 2 in the temperature range 30–60°C. The reaction product precipitated after storage of the reaction mixture for 24 h, or it was precipitated by water addition. Yields were as follows: **XVa**, 96%; **XVb**, 75%; **XVc**, 82%; **XVd**, 81%. The melting points and elemental analyses of quinone imines **XVa, b** first obtained are presented in the table.

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