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Hydrochlorination and Hydrobromination of *N*-(*N*-Arylsulfonylbenzimidoyl)-1,4-benzoquinonimines

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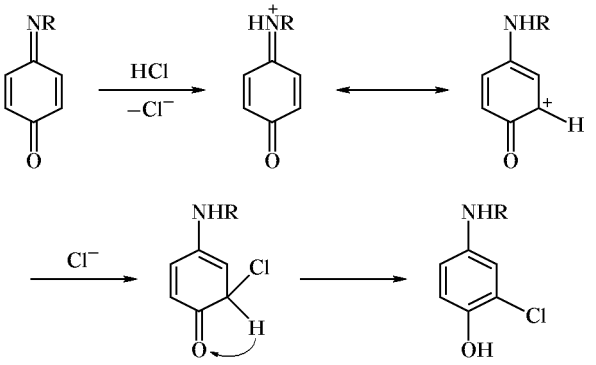
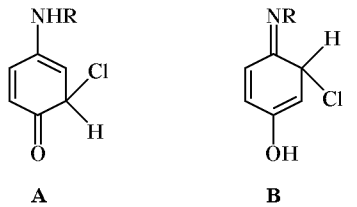
Abstract—The direction of hydrohalogenation of N-substituted *p*-quinonimines was predicted on the basis of orbital coefficients of the C^2 and C^3 atoms in the lowest unoccupied molecular orbital, calculated by the PM3 method. It was assumed that the reaction is orbital-controlled and that the initial act of hydrohalogenation is nucleophilic attack by halide ion. The proposed approach was verified by experimental hydrochlorination and hydrobromination of *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines which take up HHlg molecule following the 1,4-addition scheme, i.e., the halogen atom adds to C^2 of the quinoid ring.

Hydrochlorination of various N-substituted *p*-quinonimines has been studied in sufficient detail. In most cases chlorine adds at position *2* or *6* of the quinoid ring, i.e., the reaction follows the 1,4-addition pattern. The C^2 and C^6 atoms in *N*-substituted *p*-quinonimines are considered to be active in nucleophilic additions, specifically in hydrochlorination.

Adams and Looker [1] were the first to report on the reaction of *N*-arylsulfonyl-*p*-quinonimines with hydrogen chloride. The authors formulated a rule for chlorine orientation, according to which the initial step is protonation of the most basic center in the molecule [2]; the subsequent attack by chloride ion on position *2* of the quinoid ring is followed by prototropic rearrangement:



The protonation of *N*-substituted *p*-quinonimines in the first step of hydrochlorination is really possible. For example, protonation of *N*-aryl-1,4-benzoquinonimines yields stable solid salts [3]. However, Toropin and Burmistrov [4] found that hydrochlorination of *N*-*p*-tolyl-1,4-benzoquinonimine involves chlorine addition at C^3, i.e., according to the 6,3-addition scheme. This result suggests that protonation should not necessarily be the primary act of hydrochlorination. In order to rationalize the direction of chlorine addition to the *N*-*p*-tolyl-1,4-benzoquinonimine molecule it was proposed to estimate the energies of quinoid intermediates **A** and **B** by comparing redox potentials of 1,4-benzoquinone (E^0 = 0.583 V [5]) and *N*-*p*-tolyl-1,4-benzoquinonimine (E^0 = 0.566 V [6]) [4, 7]. Obviously, replacement of oxygen by *p*-tolylimino group reduces E^0 by 0.017 V ($|\Delta E^0|$ = 17 mV, which corresponds to an energy of 3.3 kJ/mol); therefore, structure **B** in which the *p*-tolylimino group is involved in the *ortho*-quinoid system is more favorable than structure **A** [7].



A **B**

Chlorine addition to C^3 was also observed in the hydrochlorination of *N*-*p*-methoxyphenyl- and *N*-phenyl-1,4-benzoquinonimines. The reaction with *N*-*p*-nitrophenyl-1,4-benzoquinonimine followed the 1,4-addition pattern with formation of 2-chloro derivative, whereas *N*-*p*-iodophenyl-1,4-benzoquinonimine gives rise to both 6,3- and 1,4-addition [8].

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Although *ortho*-quinoid intermediates were characterized by E^0 values for *para*-quinoid structures, the above approach turned out to be general for various *N*-substituted *p*-quinonimines [7].

The mechanism of hydrochlorination of *N*-substituted *p*-quinonimines was studied in detail by Yurchenko [9]. The results of kinetic experiments in a protic solvent (acetic acid) showed that the active species is doubly protonated quinonimine rather than its neutral form. ESR study of the reaction mixtures showed the presence of radical species, and a radical ion mechanism was proposed. In the first stage, *p*-quinonimine dication reacts with Cl^- ion to form the corresponding radical cation. Hydrochlorination products are formed as a result of a series of consecutive reactions involving radical and radical cation species [9].

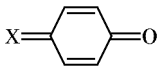
The reaction of N-substituted *p*-quinonimines with hydrogen bromide has been studied to a considerably lesser extent. The substrates were only *N*-arylsulfonyl-1,4-benzo(naphtho)quinone mono- and diimines [10, 11] and *N*-aryl-1,4-benzoquinonimines [11]. The result of hydrobromination of *N*-*p*-tolyl-1,4-benzoquinonimine was the same as in the hydrochlorination: bromine added at C^3 of the quinoid ring [11].

Taking into account that hydrohalogenation of N-substituted *p*-quinonimines is performed as a rule in an aprotic solvent ($CHCl_3$), where the probability of protonation is low (the ionizing power of chloroform is weaker than that of acetic acid), alternative hydrohalogenation mechanisms may be operative. Below we discuss one of such mechanisms, according to which chloride ion attacks neutral quinonimine as reactive species. In terms of this mechanism we can predict the site of halogen addition to the quinoid ring with no regard to redox potentials of quinonimines, which are often difficult or even impossible to determine experimentally.

We analyzed the process of hydrohalogenation of *N*-substituted *p*-quinonimines on the basis of PM3 semiempirical calculations. Comparison of the calculated energies of the lowest unoccupied molecular orbitals (LUMO) of *N*-aryl-*p*-quinonimines **I** with their redox potentials measured in [8] showed that E^0 regularly decreases as the LUMO energy rises (Table 1). This result gave us grounds to use PM3 data for further theoretical interpretations.

According to the PM3 data (Table 1), the charge on the oxygen atom in *N*-aryl-*p*-quinonimines **I** is about –0.3 a.u., whereas the charge on the nitrogen is close to zero (Tabl. 1). This means that, had the reaction been charge-controlled, the protonation would occur at the oxygen atom. However, the hydrohalogenation of *N*-(4-nitrophenyl)-1,4-benzoquinonimine follows the 1,4-addition scheme which implies initial protonation of the nitrogen atom. Taking into account that the nitrogen atom is less negative than oxygen, it is unlikely for the reaction to be charge-controlled.

Table 1. Some electronic structure parameters of *N*-aryl-1,4-benzoquinonimines **I** and 1,4-benzoquinone



X	E^0, mV	$-E_{LUMO}$, eV	$-E_{HOMO}$, eV	Charge, a.u.	
				O	N
4-$MeOC_6H_4N$	553	1.497	8.981	–0.299	0.014
4-MeC_6H_4N	566	1.503	9.196	–0.298	0.011
C_6H_5N	578	1.525	9.381	–0.297	0.008
O	583	1.706	10.921	–0.277	–
4-IC_6H_4N	596	1.615	9.054	–0.295	0.004
4-$NO_2C_6H_4N$	655	2.026	10.106	–0.284	–0.013

The orbital control of the quinonimine protonation is also improbable, for proton has a small ionic radius and the energy gap between the highest occupied molecular orbital (HOMO) of quinonimine and the vacant orbital of proton (E = 0 eV) is large (Table 1). Therefore, we can rule out protonation of quinonimine as the initial step of hydrohalogenation.

The calculated total energies (E) of intermediates **A** and **B** for *N*-aryl-1,4-quinonimines are almost similar, and comparison of their heats of formation (ΔH) indicates that intermediate **A** is always more favorable (Table 2). Therefore, formation of one or another intermediate is not crucial for the direction of hydrohalogenation. Moreover, assuming that the redox potential of quinonimine determines the mode of hydrogen halide addition, we cannot rationalize the formation of a mixture of 1,4- and 6,3-addition products from *N*-(4-iodophenyl)-1,4-benzoquinonimine ($|\Delta E^0|$ = 13 mV) and of only one isomer from *N*-phenyl-1,4-benzoquinonimine ($|\Delta E^0|$ = 5 mV [8]).

While analyzing the results of PM3 calculations, we have revealed an interesting relation between the squared AO coefficients of C^2 and C^3 in the LUMO of *N*-aryl-1,4-benzoquinonimines **Ia**–**Ig** (Fig. 1). It suggests that Cl^- and Br^- ions should attack C^2 in *N*-(4-nitrophenyl)-1,4-benzoquinonimine (**Ig**) and C^3 in quinonimines **Ia**–**Ic**, whereas compounds **Id**–**If** should give rise to mixtures of 2- and 3-isomers. This is fully consistent with the experimental data [8].

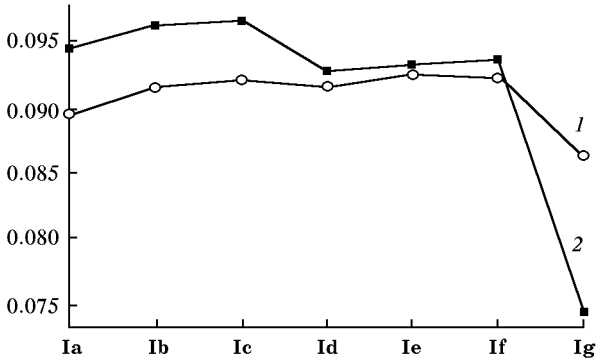


Fig. 1. PM3 orbital coefficents of (*1*) C^2 and (*2*) C^3 in the lowest unoccupied molecular orbital (LUMO) of *N*-aryl-1,4-benzoquinonimines **Ia**–**Ig**.

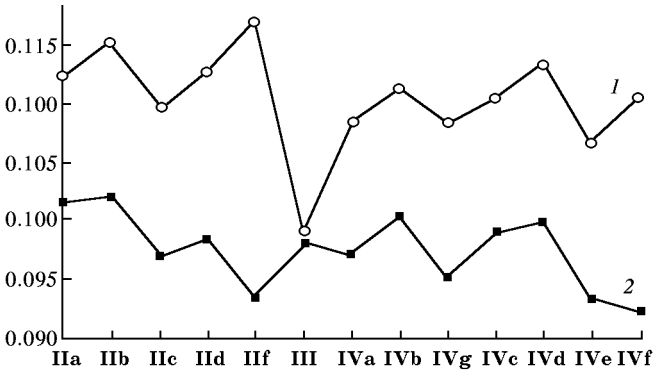
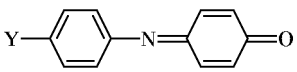


Fig. 2. PM3 orbital coefficents of (*1*) C^2 and (*2*) C^3 in the lowest unoccupied molecular orbital (LUMO) of *N*-arylsulfonyl-1,4-benzoquinonimines **IIa**–**IId** and **IIf**, *N*-acetyl-1,4-benzoquinonimine (**III**), and *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines **IVa**–**IVg**.

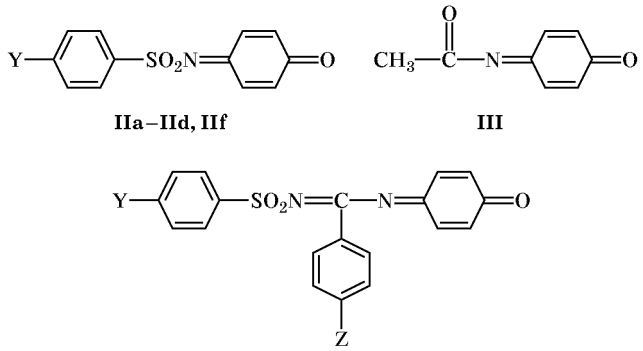
The orbital control of hydrohalogenation with initial nucleophilic attack by halide ion is supported by the small difference between the HOMO energies of Cl^- (–3.479 eV) and Br^- ions (–3.598 eV), on the one hand, and the LUMO energies of quinonimines (Table 1), on the other. We also calculated the orbital coefficients of C^2 and C^3 in the LUMO of various N-substituted *p*-quinonimines **II**–**IV** whose hydrohalogenation was studied experimentally (Fig. 2).



Ia–**Ig**

Y = CH_3O (**a**), CH_3 (**b**), H (**c**), Cl (**d**), Br (**e**), I (**f**), NO_2 (**g**).

According to the calculation results, the hydrohalogenation of *N*-arylsulfonyl-1,4-benzoquinonimines **IIa**–**IId** and **IIf** with HCl or HBr should follow the 1,4-addition scheme, which is in full agreement with the experimental data [1, 10, 12]. *N*-Acetyl-1,4-benzoquinonimine **III** should also take up halogen at position *2* of the quinoid ring; however, the formation of a mixture of two isomers cannot be ruled out, for the orbital coefficients of C^2 and C^3 approach each other. We failed to obtain *N*-acetyl-1,4-benzoquinonimine (**III**) containing no substituent in the quinoid ring (presumably, this compound is unstable); therefore, it was impossible to verify the above supposition experimentally. The results of hydrohalogenation of *N*-acetyl-1,4-benzoquinonimines having a substituent in the quinoid ring cannot be used for this purpose. For example, *N*-acetyl-3,5-dimethyl-1,4-benzoquinonimine takes up hydrogen chloride according to the 1,4-addition pattern, whereas *N*-acetyl-2,6-dimethyl-1,4-benzoquinonimine does not react with HCl [13].



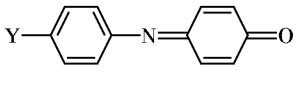
IIa–**IId, IIf** **III**

IVa–**IVg**

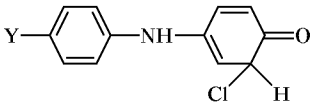
II, **IV**, Y = CH_3O (**a**), CH_3 (**b**, **g**), H (**c**), Cl (**d**), Br (**e**), NO_2 (**f**); Z = H (**a**–**f**), Cl (**g**).

Hydrohalogenation of *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines **IV** was not studied previously. We calculated the orbital coefficients of C^2 and C^3 in the LUMO of *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines **IVa**–**IVg** (Fig. 2). According to the calculations, the reactions with hydrogen chloride and hydrogen bromide should follow the 1,4-addition pattern. Our experiments confirmed the results of calculations: successive addition of two hydrogen chloride molecules (each addition process was followed by oxidation of the adduct) occurred at positions *2* and *6* of the quinoid ring of *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines **IVb**, **IVc**, **IVe**, and **IVg**. The reaction was highly regioselective. The hydrochlorination of both quinonimines **IVb**, **IVc**, **IVe**, and **IVg** and their monochloro derivatives **VIb**, **VIc**, **VIe**, and **VIg** occurred under very mild conditions, by passing gaseous hydrogen

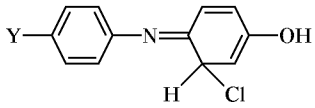
Table 2. Total energies (*E*) and heats of formation (Δ*H*) of *N*-aryl-1,4-benzoquinonimines **Ia**–**Ic**, **If**, and **Ig** and intermediate structures **A** and **B**, calculated by the PM3 method



Ia–Ic, If, Ig



A

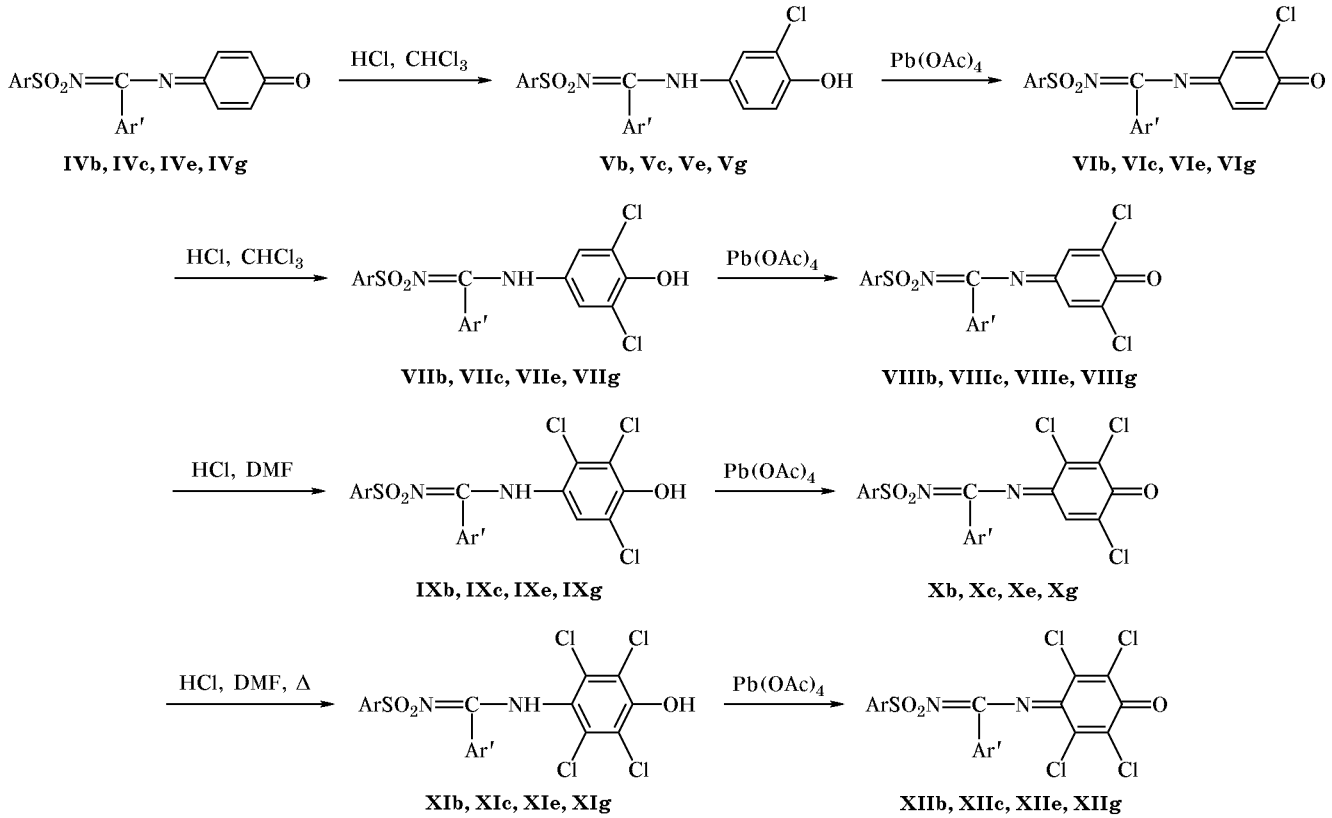


B

Y	**Ia**–**Ic**, **If**, **Ig**		**A**		**B**	
	–*E*, eV	Δ*H*, kcal/mol	–*E*, eV	Δ*H*, kcal/mol	–*E*, eV	Δ*H*, kcal/mol
CH_3O	2457.04	9.45	2790.04	–21.00	2789.71	–13.35
CH_3	2163.90	35.17	2496.85	8.25	2496.64	13.00
H	2014.18	44.61	2347.10	18.52	2346.91	22.75
I	2287.34	66.17	2620.27	39.65	2620.09	43.83
NO_2	2745.57	36.36	3078.56	8.46	3078.29	14.87

chloride through a solution of quinonimine at room temperature (Scheme 1). The third and fourth chlorine atoms can be introduced under more severe conditions. The addition of hydrogen chloride to dichloro derivatives **VIIIb**, **VIIIc**, **VIIIe**, and **VIIIg** was effected in dimethylformamide at room temperature, and the fourth HCl molecule added to compounds **Xb**, **Xc**, **Xe**, and **Xg** in dimethylformamide on heating. We previously succeeded in introducing only three chlorine atoms into *N*-arylsulfonyl-1,4-benzoquinon-

Scheme 1.



IVb, IVc, IVe, IVg → (HCl, $CHCl_3$) → **Vb, Vc, Ve, Vg** → ($Pb(OAc)_4$) → **VIb, VIc, VIe, VIg**

VIIb, VIIc, VIIe, VIIg → ($Pb(OAc)_4$) → **VIIIb, VIIIc, VIIIe, VIIIg**

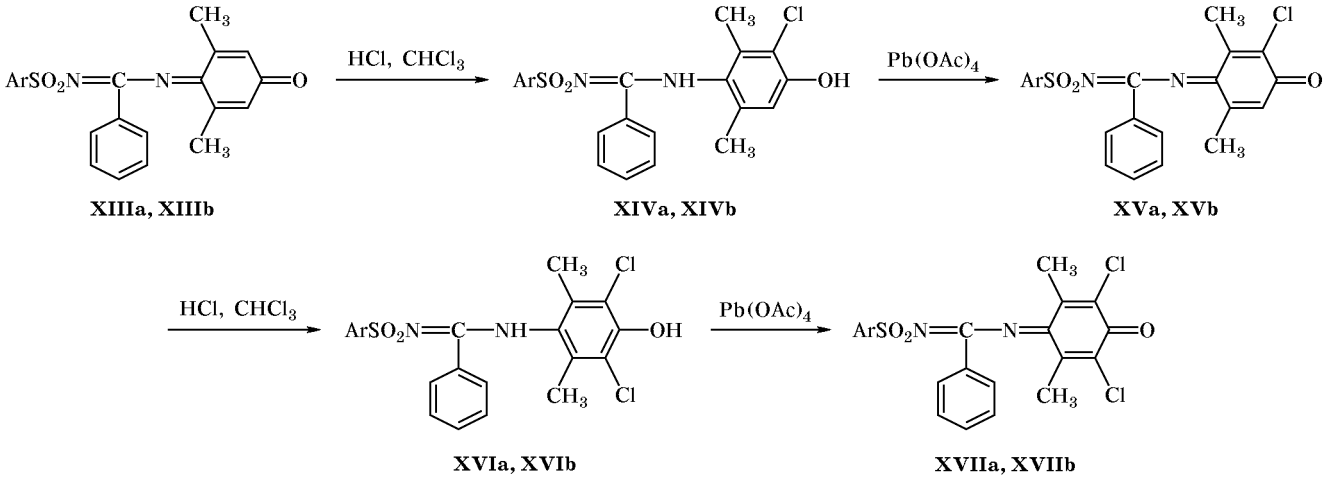
IXb, IXc, IXe, IXg → ($Pb(OAc)_4$) → **Xb, Xc, Xe, Xg**

XIb, XIc, XIe, XIg → ($Pb(OAc)_4$) → **XIIb, XIIc, XIIe, XIIg**

(HCl, DMF; HCl, DMF, Δ)

Ar = 4-$CH_3C_6H_4$ (**b**, **g**), C_6H_5 (**c**), 4-BrC_6H_4 (**e**); Ar′ = C_6H_5 (**b**, **c**, **e**), 4-ClC_6H_4 (**g**).

Scheme 2.

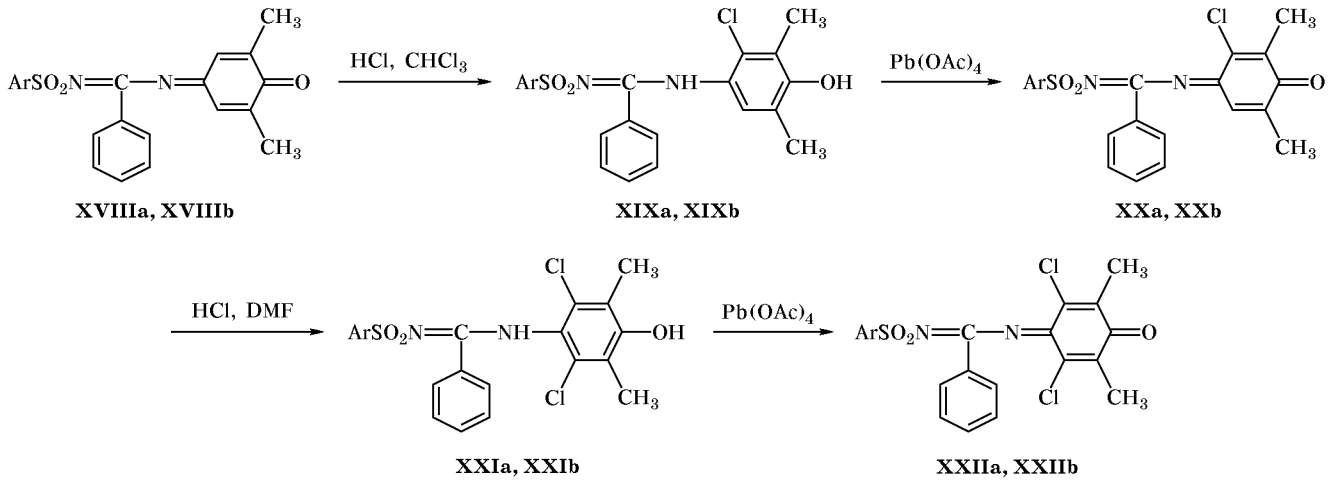


XIIIa, XIIIb **XIVa, XIVb** **XVa, XVb**

XVIa, XVIb **XVIIa, XVIIb**

Ar = C_6H_5 (**a**), 4-BrC_6H_4 (**b**).

Scheme 3.



XVIIIa, XVIIIb **XIXa, XIXb** **XXa, XXb**

XXIa, XXIb **XXIIa, XXIIb**

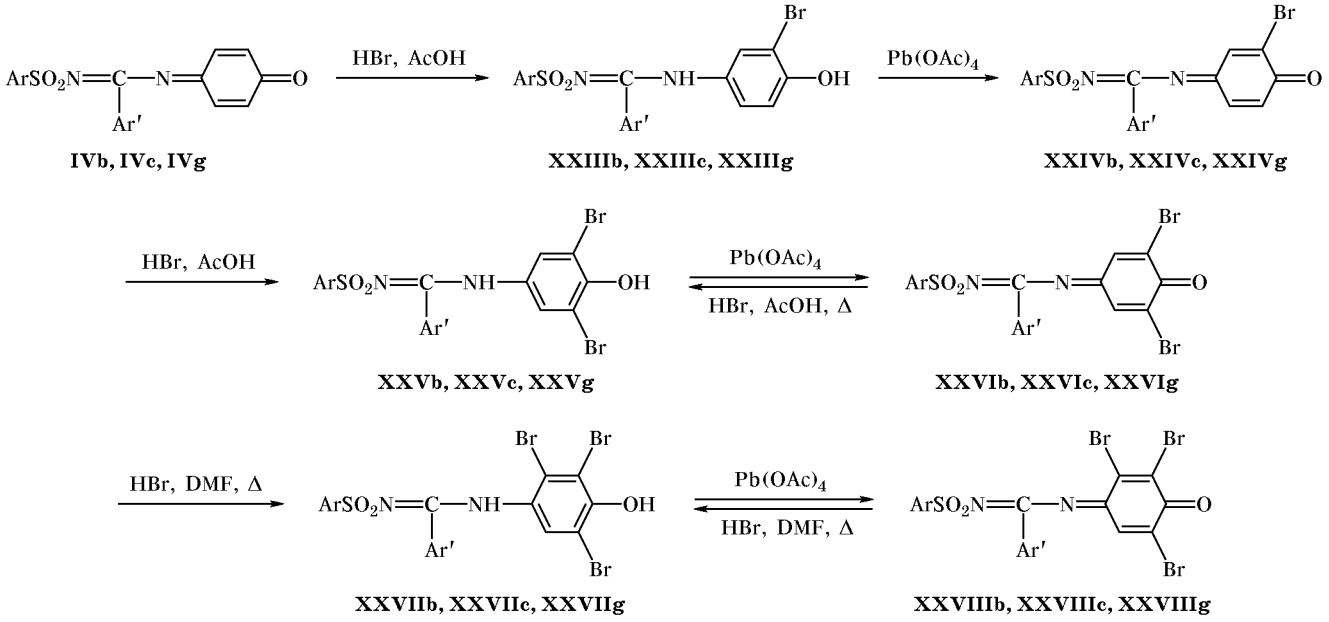
Ar = C_6H_5 (**a**), 4-BrC_6H_4 (**b**).

imine molecules [12]. Products **XIb**, **XIc**, **XIe**, and **XIg** of addition of four HCl molecules, as well as adducts **V**, **VII**, and **IX**, were oxidized to the corresponding quinonimines with lead tetraacetate in acetic acid (Scheme 1).

As might be expected, *N*-(*N*-arylsulfonylbenzimidoyl)-3,5-dimethyl-1,4-benzoquinonimines **XIIIa** and **XIIIb** took up in succession two hydrogen chloride molecules in chloroform, yielding 2,6-dichloro derivatives **XVIIa** and **XVIIb** (Scheme 2). As in the case of *N*-(*N*-arylsulfonylbenzimidoyl)-2,6-dichloro-1,4-benzoquinonimines **VIII**, the addition of one hydrogen chloride molecule to *N*-(*N*-arylsulfonylbenzimidoyl)-2,6-dimethyl-1,4-benzoquinonimines **XVIIIa** and **XVIIIb** was presumed to occur under more severe conditions (in dimethylformamide), and the second HCl molecule was expected to add to compounds **XVIII** in dimethylformamide on heating. However, the first addition readily occurred in chloroform, and the second, in dimethylformamide at room temperature (Scheme 3).

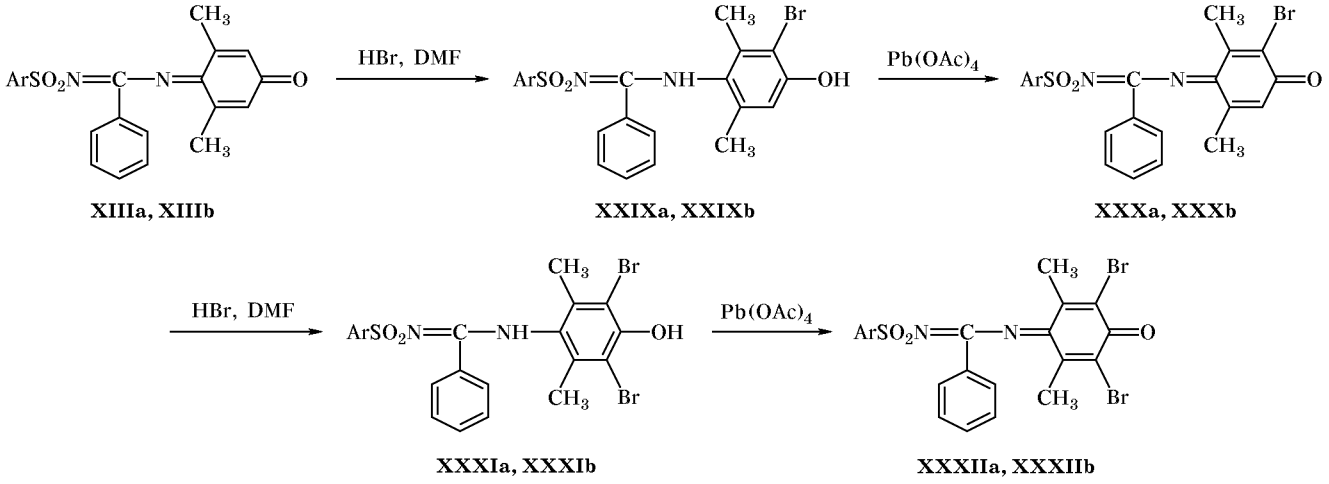
The structure of compounds **V**–**XII**, **XIV**–**XVII**, and **XIX**–**XXII** was proved by elemental analyses (Table 3) and ^1H and ^{13}C NMR spectra. The NMR spectra were recorded only for quinoid compounds **VI**, **VIII**, **X**, **XII**, **XV**, **XVII**, **XX**, and **XXII** as the most informative. The ^1H NMR spectra of **VIb**, **VIe**, **VIIIb**, **VIIIc**, **Xb**, **Xg**, **XIIg**, **XVb**, **XVIIb**, **XXb**,

Scheme 4.



Ar = 4-$CH_3C_6H_5$ (**b**, **g**), C_6H_5 (**c**); Ar′ = C_6H_5 (**b**, **c**), 4-ClC_6H_4 (**g**).

Scheme 5.



Ar = C_6H_5 (**a**), 4-BrC_6H_4 (**b**).

and **XXIIb** were fully consistent with the proposed structures (Table 4). The ^{13}C NMR spectra of **VIe**, **VIIIe**, **XIIb**, **XIIe**, **XVIIb**, **XXIIa**, and **XXIIb** contain characteristic signals from carbon atoms of the carbonyl group and benzimidoyl and quinonimine C=N groups at δ_C 169–182, 163–168, and 144–156 ppm, respectively. The other carbon signals were in agreement with the proposed structures (Table 5).

Unlike hydrochlorination, only three bromine atoms can be introduced into the quinoid ring by successive hydrobromination of *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines **IVb**, **IVc**, and **IVg** (Scheme 4). The first two HBr molecules add in acetic acid at room temperature according to the 1,4-scheme. *N*-(*N*-Arylsulfonylbenzimidoyl)-2,6-dibromo-1,4-benzoquinonimines **XXVIb**, **XXVIc**, and **XXVIg** are reduced to compounds **XXVb**, **XXVc**, and **XXVg** by the action of hydrogen bromide in acetic acid on heating; the third HBr molecule adds in dimethylformamide on heating. Oxidation of tribromo

Table 3. Yields, melting points, and elemental analyses of compounds **V**–**XII**, **XIV**–**XVII**, **XIX**–**XXII**, **XXIII**–**XXVI**, **XXVII**, **XXVIII**, and **XXIX**–**XXXII**

Comp. no.	Yield, %	mp,[a] °C	Found Hlg, %	Formula	Calculated Hlg, %
Vb	90	215	8.93, 9.04	$C_{20}H_{17}ClN_2O_3S$	8.84
Vc	88	220	8.99, 9.11	$C_{19}H_{15}ClN_2O_3S$	9.16
Ve	64	195	24.42, 24.88	$C_{19}H_{14}BrClN_2O_3S$	24.77
Vg	71	228	15.73, 15.94	$C_{20}H_{16}Cl_2N_2O_3S$	16.29
VIb	51	135	8.61, 8.65	$C_{20}H_{15}ClN_2O_3S$	8.89
VIc	69	183	9.06, 9.13	$C_{19}H_{13}ClN_2O_3S$	9.21
VIe	77	127	24.17, 24.31	$C_{19}H_{12}BrClN_2O_3S$	24.87
VIg	50	147	15.79, 15.98	$C_{20}H_{14}Cl_2N_2O_3S$	16.36
VIIb	80	205	15.84, 16.03	$C_{20}H_{16}Cl_2N_2O_3S$	16.29
VIIc	91	182	16.07, 16.52	$C_{19}H_{14}Cl_2N_2O_3S$	16.83
VIIe	90	210	30.07, 30.29	$C_{19}H_{13}BrCl_2N_2O_3S$	30.15
VIIg	56	268	22.15, 22.44	$C_{20}H_{15}Cl_3N_2O_3S$	22.64
VIIIb	83	160	16.05, 16.31	$C_{20}H_{14}Cl_2N_2O_3S$	16.36
VIIIc	75	181	16.74, 16.77	$C_{19}H_{12}Cl_2N_2O_3S$	16.91
VIIIe	91	187	29.63, 29.85	$C_{19}H_{11}BrCl_2N_2O_3S$	30.27
VIIIg	56	185	22.13, 22.37	$C_{20}H_{13}Cl_3N_2O_3S$	22.74
IXb	63	210	22.31, 22.44	$C_{20}H_{15}Cl_3N_2O_3S$	22.64
IXc	95	235	22.94, 23.16	$C_{19}H_{13}Cl_3N_2O_3S$	23.34
IXe	83	220	34.01, 34.44	$C_{19}H_{12}BrCl_3N_2O_3S$	34.84
IXg	75	235	27.86, 27.97	$C_{20}H_{14}Cl_4N_2O_3S$	28.13
Xb	89	212	22.18, 22.38	$C_{20}H_{13}Cl_3N_2O_3S$	22.74
Xc	90	210	22.90, 23.19	$C_{19}H_{11}Cl_3N_2O_3S$	23.44
Xe	63	187	34.22, 34.76	$C_{19}H_{10}BrCl_3N_2O_3S$	34.97
Xg	60	220	27.77, 27.96	$C_{20}H_{12}Cl_4N_2O_3S$	28.24
XIb	85	275	27.55, 27.93	$C_{20}H_{14}Cl_4N_2O_3S$	28.13
XIc	66	284	28.08, 28.45	$C_{19}H_{12}Cl_4N_2O_3S$	28.93
XIe	84	290	38.19, 38.72	$C_{19}H_{11}BrCl_4N_2O_3S$	38.96
XIg	67	295	32.64, 32.87	$C_{20}H_{13}Cl_5N_2O_3S$	32.91
XIIb	51	203	27.88, 27.93	$C_{20}H_{12}Cl_4N_2O_3S$	28.24
XIIc	55	235	28.74, 28.83	$C_{19}H_{10}Cl_4N_2O_3S$	29.05
XIIe	40	215	24.91, 24.97	$C_{19}H_9BrCl_4N_2O_3S$	25.01
XIIg	53	210	32.44. 32.63	$C_{20}H_{11}Cl_5N_2O_3S$	33.03
XIVa	57	291	8.34, 8.47	$C_{21}H_{19}ClN_2O_3S$	8.54
XIVb	86	280	22.98, 23.25	$C_{21}H_{18}BrClN_2O_3S$	23.36
XVa	77	164	8.36, 8.51	$C_{21}H_{17}ClN_2O_3S$	8.59
XVb	74	170	23.00, 23.17	$C_{21}H_{16}BrClN_2O_3S$	23.46
XVIa	69	303	15.61, 15.72	$C_{21}H_{16}Cl_2N_2O_3S$	15.85
XVIb	80	315	28.13, 28.21	$C_{21}H_{17}BrCl_2N_2O_3S$	28.55
XVIIa	63	191	15.66, 15.73	$C_{21}H_{14}Cl_2N_2O_3S$	15.92
XVIIb	40	227	28.37, 28.46	$C_{21}H_{15}BrCl_2N_2O_3S$	28.66
XIXa	68	302	8.35, 8.42	$C_{21}H_{19}ClN_2O_3S$	8.54
XIXb	57	210	22.95, 23.16	$C_{21}H_{18}BrClN_2O_3S$	23.36
XXa	50	173	8.36, 8.47	$C_{21}H_{17}ClN_2O_3S$	8.59
XXb	86	195	23.01, 23.32	$C_{21}H_{16}BrClN_2O_3S$	23.46
XXIa	92	276	15.45, 15.62	$C_{21}H_{16}Cl_2N_2O_3S$	15.85
XXIb	51	300	28.04, 28.37	$C_{21}H_{17}BrCl_2N_2O_3S$	28.55
XXIIa	52	212	15.46, 15.58	$C_{21}H_{14}Cl_2N_2O_3S$	15.92
XXIIb	50	190	28.19, 28.31	$C_{21}H_{15}BrCl_2N_2O_3S$	28.66

Table 3. (Contd.)

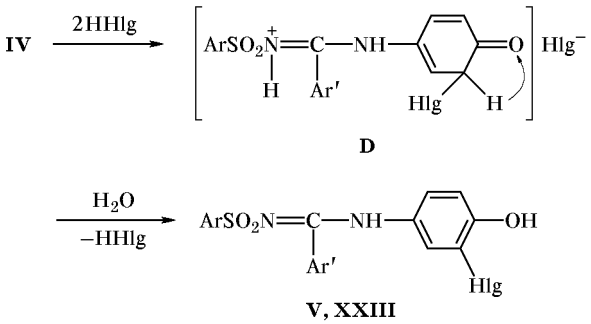
Comp. no.	Yield, %	mp,[a] °C	Found Hlg, %	Formula	Calculated Hlg, %
XXIIIb	65	198	17.68, 17.89	$C_{20}H_{17}BrN_2O_3S$	17.94
XXIIIc	91	225	18.43, 18.59	$C_{19}H_{15}BrN_2O_3S$	18.53
XXIIIg	78	225	31.42, 31.74	$C_{20}H_{16}BrClN_2O_3S$	31.43
XXIVb	63	140	18.01, 18.22	$C_{20}H_{15}BrN_2O_3S$	18.02
XXIVc	94	180	17.73, 17.95	$C_{20}H_{13}BrN_2O_3S$	18.11
XXIVg	57	162	31.22, 31.27	$C_{20}H_{14}BrClN_2O_3S$	31.57
XXVb	64	205	30.11, 30.28	$C_{20}H_{16}Br_2N_2O_3S$	30.48
XXVc	71	175	30.95, 31.24	$C_{19}H_{14}Br_2N_2O_3S$	31.32
XXVg	80	240	34.42, 34.58	$C_{20}H_{15}Br_2ClN_2O_3S$	34.95
XXVIb	58	185	30.17, 30.31	$C_{20}H_{14}Br_2N_2O_3S$	30.60
XXVIc	55	190	31.07, 31.28	$C_{19}H_{12}Br_2N_2O_3S$	31.45
XXVIg	60	192	34.67, 34.83	$C_{20}H_{13}Br_2ClN_2O_3S$	35.08
XXVIIb	43	183	39.03, 39.17	$C_{20}H_{15}Br_3N_2O_3S$	39.74
XXVIIc	67	215	40.52, 40.81	$C_{19}H_{13}Br_3N_2O_3S$	40.69
XXVIIIb	48	210	39.64, 39.82	$C_{20}H_{13}Br_3N_2O_3S$	39.88
XXVIIIc	75	215	40.59, 40.69	$C_{19}H_{11}Br_3N_2O_3S$	40.83
XXIXa	96	270	17.05, 17.22	$C_{21}H_{19}BrN_2O_3S$	17.39
XXIXb	97	280	29.36, 29.43	$C_{21}H_{18}Br_2N_2O_3S$	29.69
XXXa	77	173	17.23, 17.32	$C_{21}H_{17}BrN_2O_3S$	17.47
XXXb	91	208	29.70, 29.82	$C_{21}H_{16}Br_2N_2O_3S$	29.80
XXXIa	83	268	29.31, 29.45	$C_{21}H_{18}Br_2N_2O_3S$	29.69
XXXIb	86	312	38.82, 38.97	$C_{21}H_{17}Br_3N_2O_3S$	38.84
XXXIIa	82	205	29.18, 29.44	$C_{21}H_{16}Br_2N_2O_3S$	29.80
XXXIIb	59	230	38.91, 40.16	$C_{21}H_{15}Br_3N_2O_3S$	38.97

[a] All products were recrystallized from acetic acid.

derivatives **XXVIIb** and **XXVIIc** yields the corresponding quinonimines **XXVIIIb** and **XXVIIIc**. Our attempt to effect addition of the fourth HBr molecule resulted in reduction of **XXVIII** to tribromoaminophenols **XXVII** (Scheme 4).

N-(*N*-Arylsulfonylbenzimidoyl)-3,5-dimethyl-1,4-benzoquinonimines **XIIIa** and **XIIIb** take up in succession two HBr molecules. The addition occurs only on heating in dimethylformamide (Scheme 5). We failed to effect addition of hydrogen bromide to *N*-(*N*-arylsulfonylbenzimidoyl)-2,6-dimethyl-1,4-benzoquinonimines **XVIIIa** and **XVIIIb** even under severe conditions; as a result, only initial products and those formed by hydrolysis were isolated. The adducts obtained by reactions of quinonimines with hydrogen bromide were then oxidized with lead tetraacetate in acetic acid. The structure of compounds **XXIII**–**XXXII** was proved by elemental analyses (Table 3) and ^{1}H NMR spectra which were obtained for quinoid structures **XXVIb** and **XXVIIIb** (Table 4).

The hydrohalogenation of *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines **IV**, **XIII**, and **XVIII** involves initial formation of relatively stable bright yellow intermediates **D**. In most cases the lifetime of these intermediates ranges from 5 to 20 min. Taking into account possible protonation at the nitrogen atom of the arylsulfonylimino fragment, the most probable salt-like structure of intermediate **D** is shown below:



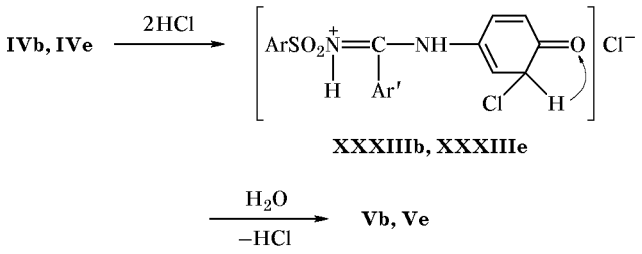
The quinoid fragment in **D** is structurally related to intermediate **A** (see above). Presumably, its stability is explained by the presence of a positive charge on the arylsylfonylimino nitrogen atom. The salt-like

Table 4. ^{1}H NMR spectra of compounds **VIb**, **VIe**, **VIIIb**, **VIIIc**, **VIIIe**, **Xb**, **Xg**, **XIIg**, **XVb**, **XVIIb**, **XXb**, **XXIIb**, **XXVIb**, and **XXVIIIb**

Comp. no.	Chemical shifts δ, ppm ($CDCl_3$)		
	quinoid ring	Ar′C=N	4-$XC_6H_4SO_2$
VIb	6.78 d (1H, 6-H), 7.16 d (1H, 3-H), 7.04 d.d (1H, 5-H)	7.42–7.80 m (5H)	7.31–7.86 d.d (4H), 2.44 s (3H, CH_3)
VIe	7.21 d (1H, 3-H), 7.05 d.d (1H, 5-H), 6.82 d (1H, 6-H)	7.44–7.79 m (5H)	7.67–7.86 d.d (4H)
VIIIb	7.19 s (2H, 3-H, 5-H)	7.43–7.79 m (5H)	7.31–7.87 d.d (4H), 2.44 s (3H, CH_3)
VIIIc	7.22 s (2H, 3-H, 5-H)	7.44–7.80 m (5H)	7.53–8.00 m (5H)
VIIIe	7.23 s (2H, 3-H, 5-H)	7.45–7.79 m (5H)	7.68–7.87 d.d (4H)
Xb	6.99 s (1H, 5-H)	7.44–7.80 m (5H)	7.32–7.87 d.d (4H), 2.44 s (3H, CH_3)
Xg	6.97 s (1H, 5-H)	7.42–7.74 d.d (4H)	7.32–7.85 d.d (4H), 2.44 s (3H, CH_3)
XIIg	–	7.42–7.71 d.d (4H)	7.33–7.92 d.d (4H), 2.45 s (3H, CH_3)
XVb	6.63 d (1H, 6-H), 2.12 d (3H, 5-CH_3), 2.29 s (3H, 3-CH_3)	7.46–7.77 m (5H)	7.66–7.87 d.d (4H)
XVIIb	2.29 s (6H, CH_3)	7.46–7.76 m (5H)	7.67–7.86 d.d (4H)
XXb	6.55 d (1H, 5-H), 2.02 s (3H, 6-CH_3), 2.30 s (3H, 2-CH_3)	7.43–7.82 m (5H)	7.64–7.87 d.d (4H)
XXIIb	2.29 s (6H, CH_3)	7.41–7.79 m (5H)	7.62–7.86 d.d (4H)
XXVIb	7.46 s (2H, 3-H, 5-H)	7.43–7.80 m (5H)	7.32–7.87 d.d (4H), 2.44 s (3H, CH_3)
XXVIIIb	7.27 s (1H, 5-H)	7.45–7.78 m (5H)	7.31–7.87 d.d (4H), 2.43 s (3H, CH_3)

structure decomposes by the action of water to form benzoid structure, 2-halo-4-aminophenol **V** or **XXIII**, via proton transfer. This process is accompanied by liberation of 1 equiv of hydrogen halide which was quantitated by the weight of silver halide formed in reaction with silver nitrate.

In two cases, namely in the hydrochlorination of *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines **IVb** and **IVe**, we succeeded in isolating stable intermediate compounds **XXXIIIb** and **XXXIIIe** (**D**):



We failed to record their ^{1}H NMR spectra, but the IR spectra of **XXXIIIb** and **XXXIIIe** contained a characteristic absorption band at 1630–1640 cm^{-1} due to carbonyl group and two bands in the regions 3170–3180 and 3290–300 cm^{-1}, which are typical of N–H bonds.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr. The ^{1}H and ^{13}C NMR spectra were obtained on a Varian VXR-300 instrument operating at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C; chloroform-*d* was used as solvent, and tetramethylsilane, as internal reference. Thin-layer chromatography was performed on Silufol UV-254 plates. Samples were applied from solutions in chloroform, and benzene–ethyl acetate (10:1) was used as eluent. The spots were visualized with UV light. Initial compounds **IVb**, **IVc**, **IVe**, **IVg**, **XIIIa**, **XIIIb**, **XVIIIa**, and **XVIIIb** were synthesized as described in [14].

***N*-(*N*-Arylsulfonylbenzimidoyl)-4-amino-2-chlorophenols Vb, Vc, Ve, and Vg; *N*-(*N*-arylsulfonylbenzimidoyl)-2,6-dichloro-4-aminophenols VIIb, VIIc, VIIe, and VIIg; *N*-(*N*-arylsulfonylbenzimidoyl)-4-amino-2-chloro-3,5-dimethylphenols XIVa and XIVb; *N*-(*N*-arylsulfonylbenzimidoyl)-4-amino-2,6-dichloro-3,5-dimethylphenols XVIa and XVIb; and *N*-(*N*-arylsulfonylbenzimidoyl)-4-amino-3-chloro-2,6-dimethylphenols XIXa and XIXb.** A stream of gaseous hydrogen chloride was passed over a period of 20–30 min through a solution of 0.01 mol of appropriate quinonimine **IVb**, **IVc**,

Table 5. ^{13}C NMR spectra (δ_C, ppm) of compounds **VIe**, **VIIIe**, **XIIb**, **XIIe**, **XVIIb**, **XXIIa**, and **XXIIb** in $CDCl_3$

Comp. no.	Quinonimine fragment									
	C^1 (C=O)	C^2	2-CH_3	C^6	6-CH_3	C^3	3-CH_3	C^5	5-CH_3	C^4 (C=N)
VIe	178.25	142.04	–	134.64	–	135.17	–	131.98	–	156.00
VIIIe	172.15	141.28	–	141.28	–	132.26	–	132.26	–	154.42
XIIb[a]	169.31	139.16	–	139.16	–	138.92	–	138.92	–	143.92
XIIe	169.22	139.17	–	139.17	–	139.05	–	139.05	–	144.55
XVIIb	171.59	138.83	–	138.83	–	141.66	16.72	141.66	16.72	152.54
XXIIa	181.73	141.40	14.66	141.40	14.66	138.26	–	138.26	–	146.08
XXIIb	181.64	141.60	14.67	141.60	14.67	138.14	–	138.14	–	146.19

Comp. no.	Ar′–C=N					$ArSO_2$			
	C=N	C^1	C^2, C^6	C^3, C^5	C^4	C^1	C^2, C^6	C^3, C^5	C^4
VIe	168.07	131.33	129.21	129.13	134.71	140.06	128.94	132.22	128.13
VIIIe	167.69	131.16	129.29	129.16	134.79	139.94	128.91	132.10	128.24
XIIb[a]	163.62	131.40	129.58	129.10	134.66	139.34	128.55	134.03	127.45
XIIe	164.20	131.17	129.21	128.90	134.29	139.86	128.62	132.28	128.18
XVIIb	163.56	130.65	129.37	128.56	134.23	140.42	128.37	132.20	127.79
XXIIa	164.90	132.14	128.86	128.77	133.56	141.12	127.34	128.57	132.66
XXIIb	165.13	132.02	129.17	128.94	133.72	140.27	128.61	132.09	127.73

[a] δ_C 21.59 ppm (CH_3 in $CH_3C_6H_4SO_2$).

IVe, **IVg**, **VIb**, **VIc**, **VIe**, **VIg**, **XIIIa**, **XIIIb**, **XVa**, **XVb**, **XVIIIa**, or **XVIIIb** in 5 ml of dry chloroform. The solution lightened, and a bright yellow solid precipitated. The product was filtered off on exposure to air, and it became colorless. It was washed with a small amount of acetic acid, dried, and recrystallized from acetic acid. The yields, melting points, and elemental analyses (for halogen) of the products are given in Table 3.

***N*-(*N*-Arylsulfonylbenzimidoyl)-4-amino-2,3,6-trichlorophenols IXb, IXc, IXe, and IXg and *N*-(*N*-arylsulfonylbenzimidoyl)-4-amino-3,5-dichloro-2,6-dimethylphenols XXIa and XXIb.** Gaseous hydrogen chloride was passed over a period of 40–45 min through a solution of 5 mmol of quinonimine **VIIIb**, **VIIIc**, **VIIIe**, **VIIIg**, **XXa**, or **XXb** in 5 ml of dimethylformamide until the solution turned colorless. The reaction was exothermic, and the mixture warmed up during the process. The mixture was cooled and diluted with 5 ml of aqueous acetic acid (1:1), and the colorless precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid (Table 3).

***N*-(*N*-Arylsulfonylbenzimidoyl)-4-amino-2,3,5,6-tetrachlorophenols XIb, XIc, XIe, and XIg.** Dry gaseous hydrogen chloride was passed over a period of 30–40 min through a solution of 5 mmol of quinonimine **Xb**, **Xc**, **Xe**, or **Xg** in 5 ml of dimethylformamide, preliminarily heated to 60–70°C. The solution lightened, and a yellow solid precipitated and quickly turned colorless. The product was filtered off, washed with acetic acid, dried, and recrystallized from acetic acid (Table 3).

Chlorinated *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines VIb, VIc, VIe, VIg, VIIIb, VIIIc, VIIIe, VIIIg, Xb, Xc, Xe, Xg, XIIb, XIIc, XIIe, XIIg, XVa, XVb, XVIIa, XVIIb, XXa, XXb, XXIIa, and XXIIb. Lead tetraacetate, 6.5 mmol, was added with stirring at room temperature to 5 mmol of aminophenol **Vb**, **Vc**, **Ve**, **Vg**, **VIIb**, **VIIc**, **VIIe**, **VIIg**, **IXb**, **IXc**, **IXe**, **IXg**, **XIb**, **XIc**, **XIe**, **XIg**, **XIVa**, **XIVb**, **XVIa**, **XVIb**, **XIXa**, **XIXb**, **XXIa**, or **XXIb** in 10 ml of acetic acid. the reaction was exothermic, and it was necessary to cool the reaction mixture. Ethylene glycol, 2 ml, was added, the mixture was stirred for 2 min, and the precipitate was filtered off, washed with methanol, dried, and recrystallized from acetic acid (Table 3).

***N*-(*N*-Arylsulfonylbenzimidoyl)-4-amino-2-bromophenols XXIIIb, XXIIIc, and XXIIIg and *N*-(*N*-arylsulfonylbenzimidoyl)-4-amino-2,6-dibromophenols XXVb, XXVc, and XXVg.** To a solu-

tion of 0.01 mol of quinonimine **IVb**, **IVc**, **IVg**, **XXIVb**, **XXIVc**, or **XXIVg** in 10 ml of acetic acid we added with stirring in portions 2 ml of 46% hydrobromic acid. The solution turned first bright yellow and then (on further stirring and cooling) lightened, and a yellow solid precipitated. The product was filtered off (it became colorless during filtration in air), dried, and recrystallized from acetic acid (Table 3).

***N*-(*N*-Arylsulfonylbenzimidoyl)-4-amino-2,3,6-tribromophenols XXVIIb and XXVIIc; *N*-(*N*-arylsulfonylbenzimidoyl)-4-amino-2-bromo-3,5-dimethylphenols XXIXa and XXIXb; and *N*-(*N*-arylsulfonylbenzimidoyl)-4-amino-2,6-dibromo-3,5-dimethylphenols XXXIa and XXXIb.** To a solution of 0.01 mol of quinonimine **XIIIa**, **XIIIb**, **XXVIb**, **XXVIc**, **XXXa**, or **XXXb** in 30 ml of DMF, heated to 110°C (**XXVIb** and **XXVIc**) or 70°C (**XIIIa**, **XIIIb**, **XXXa**, and **XXXb**), we added with stirring 10 ml of 46% hydrobromic acid. The mixture was stirred for 5 min, and it turned orange. The mixture was cooled and diluted with 20 ml of water (in the reactions with compounds **XIIIb**, **XXXa**, and **XXXb**, the product separated from the solution without dilution), and the colorless precipitate was filtered off and recrystallized from acetic acid (Table 3).

Brominated *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines XXIVb, XXIVc, XXIVg, XXVIb, XXVIc, XXVIg, XXVIIIb, XXVIIIc, XXXa, XXXb, XXXIIa, and XXXIIb were obtained from the corresponding aminophenols (**XXIIIb**, **XXIIIc**, **XXIIIg**, **XXVb**, **XXVc**, **XXVg**, **XXVIIb**, **XXVIIc**, **XXIXa**, **XXIXab**, **XXXIa**, and **XXXIb**) by the procedure described above for the chlorinated analogs, by oxidation with lead tetraacetate in acetic acid (Table 3).

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