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Chlorination of N-acyl Derivatives of *p*-Aminophenols (Naphthols) and *p*-Phenylenediamines

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Abstract—The chlorination of *N*-acyl derivatives of *p*-aminophenols can provide either *N*-acyl-2,3,6-trichloro-4-aminophenols or *N*-acyl-2,3,5,6-tetrachloro-1,4-benzoquinone imines depending on solvent nature, process temperature, and molar ratio initial compound–chlorine. The chlorination of *N*-acyl-4-amino-1-naphthols affords only *N*-acyl-2,3-dichloro-1,4-naphthoquinone imines. *N*,*N*'-Diacyl-1,4-phenylenediamines give rise on chlorination to a mixture of 2,5-dichloro-, 2,6-dichloro-, and 2,3-dichloro-*N*,*N*'-diacyl-1,4-phenylenediamines.

N-Acetyl-4-aminophenol (Paracetamol) is an efficient analgetic. Its oxidation product, *N*-acetyl-1,4-benzoquinone imine is an intermediate in the transformations sequence ensuring low toxicity of the Paracetamol [1]. Therefore the investigation of N-acyl derivatives of *p*-aminophenol (naphthol) and *p*-phenylenediamine, and of their oxidation products, the corresponding quinone imines, is of obvious interest.

It was reported [1] that depending on reaction conditions the chlorination of *N*-acetyl-4-aminophenol gave rise to *N*-acetyl-2,3,5,6-tetrachloro-4-aminophenol or to *N*-acetyl-2,3,5,6-tetrachloro-1,4-benzoquinone imine. The chlorination of *N*,*N*'-di-*p*-toluoyl-1,4-phenylenediamine [2] was presumed to afford *N*,*N*'-di-*p*-toluoyl-2,5-dichloro-1,4-phenylenediamine; yet the location of chlorine atoms in the molecule was not proved.

The successive hydrochlorination and oxidation of *N*,*N*'-dibenzoyl-1,4-benzoquinone diimine is known to provide as final product *N*,*N*'-dibenzoyl-2,3,5-trichloro-1,4-benzoquinone diimine [3]. The *N*,*N*'-dibenzoyl-2,3,5,6-tetrachloro-1,4-benzoquinone diimine was prepared starting with 2,3,5,6-tetrachloro-1,4-phenylenediamine [3].

In systematic investigation of chlorination of *N*-arylsulfonyl derivatives of 1,4-benzo(naphtho)-quinone monoimines and diimines and the reduced forms thereof we obtained numerous chlorinated derivatives of the above compounds depending on the reaction conditions [4–7]. Therefore in the present study we concentrated on chlorination of *N*-acyl derivatives of *p*-aminophenols(naphthols) and *p*-phenylenediamines.

The chlorination of *N*-acyl-4-aminophenols was performed with the use of chlorine gas. We used as solvents acetic acid, DMF, a mixture acetic acid–DMF (5 : 1), chloroform, and tetrachloromethane. Disregarding the character of solvent unlike the chlorination of *N*-arylsulfonyl-4-aminophenols [4] the first products isolated from the reaction mixture after treating *N*-acetyl(aroyl)-4-aminophenols (**Ia–e**) with chlorine were *N*-acetyl(aroyl)-2,3,6-trichloro-4-aminophenols (**IIa–e**) (Scheme 1).

On decreasing the ratio aminophenol–chlorine we failed to obtain the chlorination products containing one or two chlorine atoms in the molecule: just was reduced the yield of the trichloro derivatives **IIa–e**, or the chlorination failed to occur, and the initial compounds were recovered.

Compounds **IIa–e** of the highest purity were obtained at chlorination in the acetic acid or its mixture with DMF (5 : 1).

In DMF occurred deeper chlorination. In all cases at certain ratios initial compound–chlorine were obtained *N*-acetyl(aroyl)-2,3,5,6-tetrachloro-1,4-benzoquinone imines (**IVa–e**). The chlorination of *N*-acetyl-4-aminophenol in DMF at the ratio aminophenol–Cl_2 1 : 4 afforded *N*-acetyl-2,3,5,6-tetrachloro-4-aminophenol (**IIIa**) in agreement with the published data [1].

The chlorination of compounds **IIa–e, IIIa** in DMF furnished *N*-acetyl(aroyl)-2,3,5,6-tetrachloro-1,4-benzoquinone imines **IVa–e**. Our attempt to attain deeper chlorination of *N*-acetyl-4-aminophenols in order to prepare semiquinoid substances similar to those obtained at chlorination of *N*-arylsulfonyl-4-

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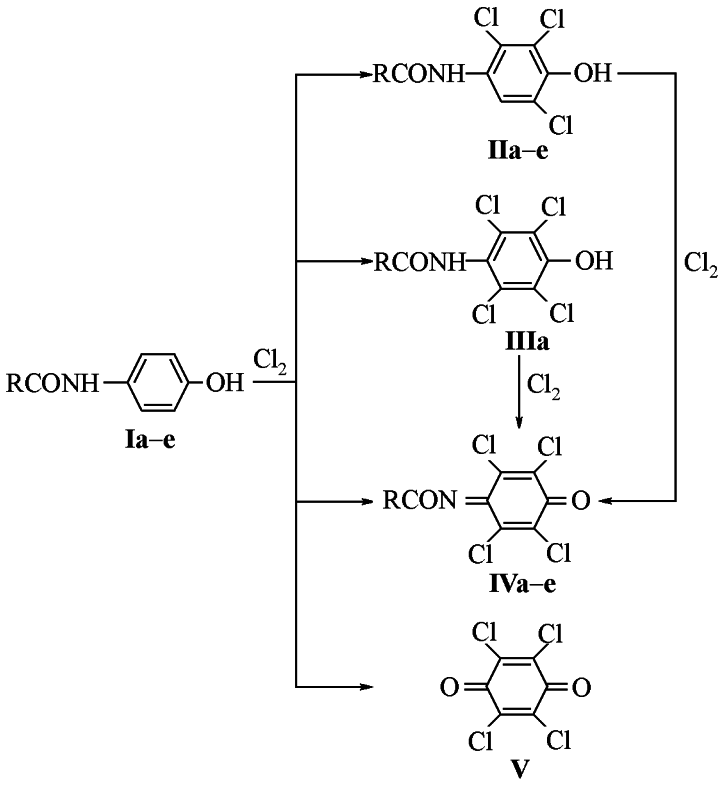
Scheme 1.



R = CH_3 (**a**), C_6H_5 (**b**), 4-$CH_3C_6H_4$ (**c**), 3-$CH_3C_6H_4$ (**d**), 4-ClC_6H_4 (**e**).

aminophenols [4] by increasing the ratio of chlorine to the initial compound was unsuccessful: In all runs we isolated only chloranil (**V**) from the reaction mixture. At longer reaction time and higher temperature alongside the main chlorination products a hydrolysis product, chloranil (**V**), appeared in the reaction mixture due to the side reaction with the air moisture. In the tetrachloromethane *N*-acyl-4-aminophenols **Ia–e** did not undergo chlorination.

The composition and structure of compounds **IIa–e, IIIa, IVa–e** were proved by elemental analysis, IR, ^1H and ^{13}C NMR spectra.

In the IR spectra of compounds **IIb–e** are present absorption bands in the regions 3400– 3250, 3330–3200, 1650–1630 cm^{-1}, characteristic of groups OH, NH, and C=O respectively, and in the IR spectra of compounds **IVb–e** in the regions 1690– 1675, 1645–1640, 1600–1590 cm^{-1}, characteristic of groups C=O (quinoid), C=O (aroyl), and C=N respectively.

In the ^1H NMR spectra of compounds **IIa–c** appear a proton singlet from H^5 in δ 7.58–7.65 range and the proton signals from groups R–CO, NH, and OH. In the ^1H NMR spectra of compounds **IVb, c, e** are observed signals from protons of R–CO groups (Table 2), and in the ^{13}C NMR spectra of compounds **IVb, c, e** appears the complete set of signals corresponding to these structures (Table 3).

The chlorination of *N*-acyl-4-amino-1-naphthols **VIa–d** was also performed with the use of chlorine gas. DMF was used as a solvent. *N*-Acyl-4-amino-1-naphthols **VIa–d** in any solvent, notwithstanding the molar ratio initial compound–chlorine and temperature, are chlorinated into *N*-acyl-2,3-dichloro-1,4-naphthoquinone imines (**VIIa–e**) (Scheme 2).

N-Aroyl-2,3-dichloro-1,4-naphthoquinone imines **VIIb–e** were stable against hydrolysis: No hydrolysis product, 2,3-dichloro-1,4-naphthoquinone was detected in the reaction mixture at the process carried out at higher temperature and at higher excess of chlorine. The hydrolysis product was found in the reaction mixture by TLC method at chlorination of *N*-acetyl-4-amino-1-naphthol (**VIa**).

The reduced amount of chlorine with respect to the initial substance did not result in formation of chlorination products containing a single chlorine atom (either in oxidized or reduced form) or a chlorinated reduced form with two chlorine atoms, only decreased the yield of compounds **VII**. At the

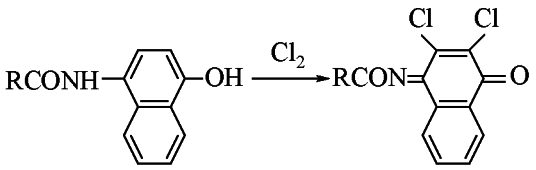
Table 1. Melting points and elemental analyses of compounds **Ic–e, IIa–e, IVb–e, VIc–d, VIIa–e,VIIId, e, IXa**

Compd. no.	mp, °C	Found, %		Formula	Calculated, %	
		Cl	N		Cl	N
Ic	207	–	5.83, 5.97	$C_{14}H_{13}NO_2$	–	6.17
Id	155	–	5.86, 6.01	$C_{14}H_{13}NO_2$	–	6.17
Ie	250		5.34, 5.43	$C_{13}H_{10}ClNO_2$		5.66
IIa	195	41.53, 41.68		$C_8H_6Cl_3NO_2$	41.79	
IIb	182	33.20, 33.37		$C_{13}H_8Cl_3NO_2$	33.59	
IIc	178	31.86, 31.99		$C_{14}H_{10}Cl_3NO_2$	32.17	
IId	208	31.72, 31.88		$C_{14}H_{10}Cl_3NO_2$	32.17	
IIe	203	39.93, 39.97		$C_{13}H_7Cl_4NO_2$	40.39	
IVb	225	40.07, 40.28		$C_{13}H_5Cl_4NO_2$	40.63	
IVc	233	39.02, 39.23		$C_{14}H_7Cl_4NO_2$	39.06	
IVd	170	38.67, 38.72		$C_{14}H_7Cl_4NO_2$	39.06	
IVe	215	45.74, 45.85		$C_{13}H_4Cl_5NO_2$	46.23	
VIc	230	–	4.58, 4.73	$C_{18}H_{15}NO_2$	–	5.02
VId	250		4.48, 4.70	$C_{17}H_{12}ClNO_2$		4.71
VIe	265	–	13.65, 13.82	$C_{17}H_{11}N_3O_6$	–	13.77
VIIa	245 (decomp.)	26.03, 26.38		$C_{12}H_7Cl_2NO_2$	26.45	
VIIb	152	21.51, 21.67		$C_{17}H_9Cl_2NO_2$	21.52	
VIIc	188	20.60, 20.92		$C_{18}H_{11}Cl_2NO_2$	20.65	
VIId	210	28.74, 29.06		$C_{17}H_8Cl_3NO_2$	29.10	
VIIe	142	16.45, 16.71		$C_{17}H_7Cl_2N_3O_6$	16.88	
VIIId	300	–	8.07, 8.19	$C_{22}H_{20}N_2O_2$	–	8.13
VIIIe	360		7.08, 7.13	$C_{20}H_{14}Cl_2N_2O_2$		7.28
IXa	295	26.71, 26.94		$C_{10}H_{10}Cl_2N_2O_2$	27.18	

ratio *N*-aroyl-4-amino-1-naphthol–chlorine equal to 1:1 no chlorination occurred.

The chlorination of *N*-acyl-4-amino-1-naphthols to only 2,6-dichloro-1,4-naphthoquinone imines whereas the *N*-acyl-4-aminophenols predominantly afford the chlorinated products of the reduced form is due to lower redox potentials of the *N*-substituted 1,4-naphthoquinone imines as compared with those of *N*-substituted 1,4-benzoquinone imines [8].

Scheme 2.



VIa–e **VIIa–e**

R = CH_3 (**a**), C_6H_5 (**b**), 4-$CH_3C_6H_4$ (**c**), 4-ClC_6H_4 (**d**), 2,4-$(NO_2)_2C_6H_3$ (**e**).

The composition and structure of compounds **VII** were proved by elemental analysis, IR, ^1H and ^{13}C NMR spectra. In the IR spectra of compounds **VIIa–e** appear absorption bands in the regions 1680–1660, 1645–1630, 1590–1585 cm^{-1} characteristic of groups C=O (quinoid), C=O (acyl), and C=N respectively. In the ^1H NMR spectra of compounds **VIIa–c** are present signals from four protons attached to the naphthalene skeleton and the proton signals from the R–CO groups (Table 2). In the ^{13}C NMR spectrum of compound **VIIb** appears a complete set of signals corresponding to its structure (Table 3).

The chlorination of *N*,*N*'-diacyl-1,4-phenylenediamines **VIIIa–e** was carried out in DMF or its mixture with acetic acid (1:5) with chlorine gas. The chlorination of *N*,*N*'-diaroyl-1,4-phenylenediamines **VIIIb–e** yields a mixture of three isomers: *N*,*N*'-diaroyl-2,5-dichloro-1,4-phenylenediamines **IXb–e**, *N*,*N*'-diaroyl-2,6-dichloro-1,4-phenylenediamines

Table 2. ^{1}H NMR Spectra of compounds **IIa–c, IIIa, IVb, c, e, VIIa–c, IXa–c, Xb, c, XIb, c, XIIb–e, XIIIb–e, XIVb–e, XV, XVI**

Compd. no. (contents in mixture, %)	Solvent	Chemical shift, δ, ppm			
		Nuclea protons	RCO protons	NH	OH
IIa	DMSO-d_6	7.65 s (1H, H^5)	2.09 s (3H, CH_3)	9.32 s	10.06 s
IIb	DMSO-d_6	7.58 s (1H, H^5)	7.49–7.99 m (5H)	9.89 s	10.35 s
IIc	DMSO-d_6	7.61 s (1H, H^5)	7.33–7.89 d.d (4H), 2.38 s (3H, CH^3)	9.87 s	10.05 s
IIIa	DMSO-d_6	–	2.11 s (3H, CH_3)	9.93 s	10.55 s
IVb	$CDCl_3$	–	7.49–7.83 m (5H)	–	–
IVc	$CDCl_3$	–	7.29–7.72 d.d (4H), 2.44 (3H, CH_3)	–	–
IVe	$CDCl_3$	–	7.47–7.78 d.d (4H)	–	–
VIIa	$CDCl_3$	8.27 q (1H, H^5), 8.16 q (1H, H^8), 7.83–7.86 m (2H, H^6, H^7)	1.62 s (3H, CH_3)	–	–
VIIb	$CDCl_3$	8.26 q (1H, H^5), 8.22 q (1H, H^8), 7.73–7.76 m (2H, H^6, H^7)	7.47–7.91 (5H)	–	–
VIIc	$CDCl_3$	8.25 q (1H, H^5), 8.20 q (1H, H^8), 7.72–7.76 m (2H, H^6, H^7)	7.28–7.80 d.d (4H), 2.44 s (3H, CH_3)	–	–
IXa	DMSO-d_6	7.89 s (2H, H^3, H^6)	2.10 s (6H, CH_3)	9.58 br.s (2H)	–
IXb (20)	DMSO-d_6	7.86 s (2H, H^3, H^6)	7.51–8.02 m (10H)	10.11 br.s (2H)	–
Xb (75)	DMSO-d_6	8.06 s (2H, H^3, H^5)	7.51–8.02 m 10H)	10.24 s 1H),	–
				10.56 s (1H)	–
XIb (5)	DMSO-d_6	7.76 s (2H, H^3, H^6)	7.51–8.02 m (10H)	10.23 br.s (2H)	–
IXc (30)	DMSO-d_6	7.85 s (2H, H^3, H^6)	7.46–8.15 d.d (8H), 2.44 s (6H, CH_3)	10.02 br.s (2H)	–
Xc (60)	DMSO-d_6	7.97 s (2H, H^3, H^5)	7.37–7.95 d.d (8H), 2.41 s (6H, CH_3)	10.47 br.s (2H)	–
Xlc (10)	DMSO-d_6	7.62 s (2H, H^5, H^6)	7.34–7.95 d.d (8H), 2.45 s (6H, CH_3)	10.33 br.s (2H)	–
XIIb (38)	$CDCl_3$	7.09 s (2H, H^3, H^6)	7.49–7.95 m (10H)	–	–
XIIIb (55)	$CDCl_3$	7.16 s (2H, H^3, H^5)	7.49–7.83 m (5H), 7.49–7.95 m (5H)	–	–
XIVb (7)	$CDCl_3$	6.74 s (2H, H^5, H^6)	7.46–7.91 m (10H)	–	–
XIIc (20)	$CDCl_3$	6.89 s (2H, H^3, H^6)	7.30–7.83 d.d (8H), 2.43 s (6H, CH_3)	–	–
XIIIc (77)	$CDCl_3$	7.12 s (2H, H^3, H^5)	7.30–7.83 d.d (8H), 2.45 s (6H, CH_3)	–	–
XIVc (3)	$CDCl_3$	6.83 s (2H, H^5, H^6)	7.30–7.83 d.d (8H), 2.46 s (6H, CH_3)	–	–
XIId (79)	$CDCl_3$	6.91 s (2H, H^3, H^6)	7.34–7.73 m (8H), 2.41 s (6H, CH_3)	–	–
XIIId (16)	$CDCl_3$	7.13 s (2H, H^3, H^5)	7.34–7.73 m (8H), 2.43 s (6H, CH_3)	–	–
XlVd (5)	$CDCl_3$	6.72 s (2H, H^5, H^6)	7.34–7.73 m (8H), 2.47 s (6H, CH_3)	–	–
XIIe (67)	$CDCl_3$	6.93 s (2H, H^3, H^6)	7.45–7.88 d.d (8H)	–	–
XIIIe (6)	$CDCl_3$	7.11 s (2H, H^3, H^5)	7.45–7.88 d.d (8H)	–	–
XIVe (27)	$CDCl_3$	6.76 s (2H, H^5, H^6)	7.45–7.88 d.d (8H)	–	–
XV	$CDCl_3$	6.92 s (4H, H^2, H^3, H^5,H^6)	7.46–7.93 m (10H)	–	–
XVI	$CDCl_3$	7.23 s (1H, $H^3$3), 6.83 s (2H, H^5, H^6)	7.47–7.93 m (10H)	–	–

Table 3. ^{13}C NMR spectra ($CDCl_3$) of *N*-aroyl-2,3,5,6-tetrachloro-1,4-benzoquinone imines (**IVb, c, d**) and *N*-benzoyl-2,3-dichloro-1,4-naphthoquinone imine (**VIIb**)

Compd. no.	Chemical shift, δ_C, ppm
IVb	174.81 (C=O aroyl), 169.45 (C=O), 142.97 (C=N), 139.39 (C^3, C^5), 138.55 (C^2, C^6), 133.94 (C^4 in ArCO), 131.71 (C^1 in ArCO), 129.01 (C^3 in ArCO), 128.80 (C^2 in ArCO)
IVc	174.79 (C=O aroyl), 169.48 (C=O), 144.99 (C=N), 142.80 (C^4 in ArCO), 139.48 (C^3, C^5), 138.46 (C^2, C^6), 129.73 (C^3 in ArCO), 129.04 (C^1 in ArCO), 128.86 (C^2 in ArCO), 21.79 (CH_3 in ArCO)
IVe	173.72 (C=O aroyl), 169.35 (C=O), 143.44 (C=N), 140.57 (C^4 in ArCO), 139.23 (C^3, C^5), 138.78 (C^2, C^6), 131.10 (C^1 in ArCO), 130.13 (C^3 in ArCO), 129.46 (C^2 in ArCO)
VIIb	176.13 (C=O aroyl), 175.71 (C=O), 146.60 (C=N), 141.55, 140.10 (C^9, C^{10}), 134.28, 132.91, 127.97, 127.64 (C^5, C^6, C^7, C^8), 133.47 (C^4 in C_6H_5CO), 132.20, 131.49 (C^2, C^3), 130.36 (C^1 in C_6H_5CO), 128.86, 128.79 (C^2, C^3 in C_6H_5CO)

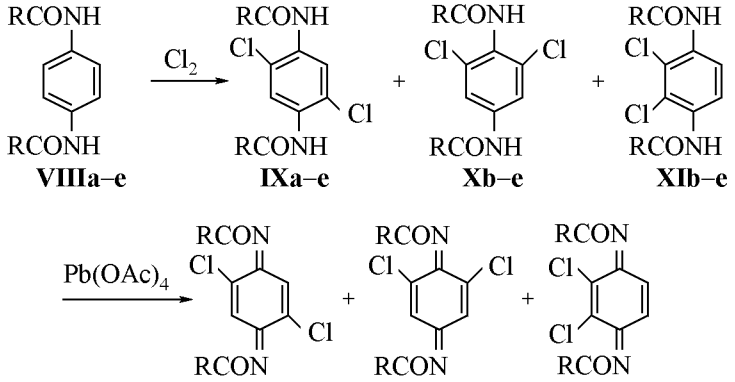
Xb–e, and *N*,*N*'-diaroyl-2,3-dichloro-1,4-phenylene diamines **XIb–e** (Scheme 3).

The content of isomers in the mixture was evaluated from the integrated signals in the ^1H NMR spectra. The elemental analyses show that in the isomer mixtures are no substances of another composition. A single isomer, *N*,*N*'-diacetyl-2,5-dichloro-1,4-phenylenediamine (**IXa**) was obtained from *N*,*N*'-diacetyl-1,4-phenylenediamine (**VIIIa**). This product was identic to a compound with the known structure [9].

We did not observe deeper chlorination of the *N*,*N*'-diacyl-1,4-phenylenediamines. It is apparently due to significantly higher redox potentials of the *p*-benzoquinone diimines as compared to those of *p*-benzoquinone monoimines [8]. Besides the chlorination process includes a stage of the quinoid structure formation; the increased number of chlorine atoms attached to the *p*-phenylenediamine ring causes growth of the redox potential, and further chlorination becomes impossible.

Since the chlorination of compounds **VIIIb–e** gave rise to a mixture of three isomers **IX, X, XI** that posed a great problem to investigation by ^1H NMR we effected oxidation of these mixtures to the corresponding quinone diimines: *N*,*N*'-diaroyl-2,5-dichloro-1,4-benzoquinone diimines **XIIb–e**, *N*,*N*'-diaroyl-2,6-dichloro-1,4-benzoquinone diimines **XIIIb–e**, *N*,*N*'-diaroyl-2,3-dichloro-1,4-benzoquinone diimines **XIVb–e** (Scheme 3). The ^1H NMR spectra of the latter compounds are more informative. In order to assign the proton signals of

Scheme 3.



R = CH_3 (**a**), C_6H_5 (**b**), 4-$CH_3C_6H_4$ (**c**), 3-$CH_3C_6H_4$ (**d**), 4-ClC_6H_4 (**e**).

the quinoid ring in the isomers we synthesized *N*,*N*'-dibenzoyl-1,4-benzoquinone diimine (**XV**) [3], *N*,*N*'-dibenzoyl-2-chloro-1,4-benzoquinone diimine (**XVI**) [3], and *N*,*N*'-dibenzoyl-2,6-dichloro-1,4-benzoquinone diimine (**XIIIb**) [3]. Their spectra are given in Table 2.

Due to the fast *Z*,*E*-isomerization (in the ^{1}H NMR time scale) of *p*-quinone imines *N*-aroyl derivatives as we have established previously [10] all the protons of the quinoid ring of compound **XV** appear in the ^{1}H NMR spectrum as a singlet, the proton H^4 neighboring to the chlorine in compound **XVI** gives a singlet at δ7.23 ppm, and to the protons H^5, H^6 belongs a common singlet at δ 6.83 ppm. The protons H^3, H^5 of compound **XIIIb** also appear as one singlet resonance at δ 7.16 ppm.

In the ^{1}H NMR spectra of isomer mixtures **XII, XIII, XIV** the signals of the quinoid ring protons appear respectively in the δ 7.11–7.16 ppm region for 2,6-dichloro derivatives **XIIIb–e**, δ 6.89–7.09 ppm for 2,5-dichloro derivatives **XIIb–e**, and δ 6.72–6.83 for 2,3-dichloro derivatives **XIVb–e**. As show the ^{1}H NMR spectra, in the mixture are usually prevailing isomers **XII** or **XIII**. Compounds **IX–XIV** were not isolated as individual substances. The analysis of the spectra of isomers **XII, XIII**, and **XIV** indicated that the compound described in [2] as *N*,*N*'-di-*p*-toluoyl-2,5-dichloro-1,4-benzoquinone diimine (**XIIc**) was really its isomer *N*,*N*'-di-p-toluoyl-2,6-dichloro-1,4-benzoquinone diimine (**XIIIc**). Thus the separated in [2] chlorination product was not *N*,*N*'-di-*p*-toluoyl-2,5-dichloro-1,4-phenylenediamine (**IXc**) but *N*,*N*'-di-*p*-toluoyl-2,6-dichloro-1,4-phenylenediamine (**Xc**).

EXPERIMENTAL

IR spectra of compounds synthesized were recorded on spectrophotometer UR 20 from KBr pellets. ^{1}H and ^{13}C NMR spectra were registered on spectrometer Varian VXR-300 at operating frequencies 300 MHz (for ^{1}H) and 75.4 MHz (for ^{13}C), TMS was used as external reference.

The reaction mixtures were analyzed by TLC on Silufol UV-254 plates; solvent chloroform, eluent benzene–hexane, 10 : 1, development in UV light.

Compounds **Ia, b, VIa, b, VIIIa–c** were prepared along procedure described in [11] by acylation of *p*-aminophenol(naphthol) and *p*-phenylenediamine with an appropriate acyl chloride in a mixture DMF–AcOH, 1 : 3. Melting points of compounds **Ia, b, VIa, b, VIIIa–c** are consistent with the published data.

In the experiments were used recrystallized substances, dried and freshly distilled solvents.

***N*-Aroyl-1,4-aminophenols(naphthols) Ic–e, VIc–e, *N*,*N*'-diaroyl-1,4-phenylenediamines VIIId, e.** To a solution of 0.5 mol of *p*-aminophenol(naphthol) or *p*-phenylenediamine and 0.5 mol of anhydrous sodium acetate in 0.5 l of DMF–AcOH mixture, 1 : 3, were added at cooling while stirring by small portions the appropriate acyl chlorides in equimolar amounts. On completing the acyl chloride addition the stirring was continued for 30 min. The precipitate was filtered off, compounds **Ic–e, VIc–e** were recrystallized from acetic acid, compounds **VIIId, e** from DMF. The yields of compounds obtained are as follows: 75% (**Ic**), 64% (**Id**), 68% (**Ie**), 55% (**VIc**), 51% (**VId**), 58% (**VIe**), 67% (**VIIId**), 62% (**VIIIe**). The melting points and elemental analyses are given in Table 1.

***N*-Aroyl(acetyl)-2,3,6-trichloro-4-aminophenols (IIa–e).** Through a solution of 0.5 g of compound **Ia–e** in 3 ml of one of solvents DMF, CH_3CO_2H, DMF–CH_3CO_2H mixture, 1 : 5, or $CHCl_3$ was passed chlorine gas at a rate 15–20 ml min^{-1} till the additional weight of the mixture corresponded to the desired molar ratio initial compound–chlorine. (a) Compounds **IIa–e** were prepared by chlorination in acetic acid in the temperature range 20–45°C at molar ratio initial compound–chlorine in the 1 : 2 to 1 : 6 range. The best yield and purity of compounds **IIa–e** were obtained at the ratio initial compound–chlorine 1 : 4 and 30–40°C. Yields of the reaction products were as follows: **IIa** 89%, **IIb, c** 51%, **IId** 31%, **IIe** 39%. (b) Compounds **Ib, c** were prepared by chlorination in DMF at 40°C and the molar ratio initial compound–chlorine 1 : 4. At these conditions yield of compound **IIb** was 72%, yield of compound **IIc** 34%. (c) The chlorination in a mixture DMF–acetic acid, 1 : 5, at 30°C and molar ratio initial compound–chlorine from 1 : 2 to 1 : 4 afforded **IIa** in 68% yield, at 35–45°C and molar ratio initial compound–chlorine from 1 : 2 to 1 : 3 furnished **IIb** in 46% yield. (d) Compounds **IIb–e** were also obtained by chlorination in $CHCl_3$ at 25°C and complete saturation of the solution with chlorine. The yields of the reaction products were as follows: **IIb** 47%, **IIb** 71%, **IId** 39%, **IIe** 46%.

In all runs to the end of the chlorination separated a precipitate that was recrystallized from acetic acid.

***N*-Acetyl(aroyl)-2,3,5,6-tetrachloro-1,4-benzoquinone imines (IVa–e).** (a) Through a solution of 0.5 g of compound **Ib–e** in 3 ml of DMF was passed chlorine gas at a rate 15–20 ml/min till the additional weight of the mixture corresponded to the desired molar ratio initial compound–chlorine, 1 : 5. The temperature was maintained in the 10–70°C range. The reaction products **IVb–e** were precipitated from the reaction mixture with water. The oily substance precipitated solidified within 24 h. The yellow solid was recrystallized from acetic acid. The highest yield was obtained with compound **IV** at 40°C (85%). The yields of the other compounds were as follows: **IVc** 58% (70°C), **IVd** 38% (70°C), **IVe** 43% (50°C). The chlorination at higher temperature and at greater excess of chlorine is accompanied by hydrolysis of the reaction product to yield chloranil (**V**).

(b) The chlorination of compounds **IIa–c, e** was carried out along the procedure described above in DMF solution at 50°C and at the ratio initial compound–chlorine 1 : 2. The reaction product was precipitated with water. The precipitates of compounds **IVa–c, e** were recrystallized from acetic acid. The yields of compounds obtained are as follows: **IVa** 63%, **IVb** 75%, **IVc** 56%, **IVe** 79%. (c) Compound **IVa** was obtained by treating with chlorine of compound **IIIa** in DMF at 30°C and molar ratio compound **IIa**–chlorine 1 : 6. The reaction product was precipitated from the reaction mixture with water, recrystallized from acetic acid, yield 67%. Compound **IVa** was identic to a substance with a known structure [1].

***N*-Aroyl(acetyl)-2,6-dichloro-1-naphthoquinone imines VIIa–e.** Through a solution of 0.5 g of compound **VIb–e** in 3 ml of DMF was passed chlorine gas at a rate 15–20 ml min^{-1} till the additional weight of the mixture corresponded to the desired molar ratio initial compound–chlorine (from 1 : 2 to 1 : 8). The temperature was maintained in the 25–65°C range. The yellow reaction products **VIIa–e** precipitated from the reaction mixture to the end of chlorination. The products were recrystallized from acetic acid. The highest yield of chlorination products was observed for compound **VIIa** at 65°C and molar ratio initial compound–chlorine 1 : 5 (41%), for compound **VIIb** at 45°C and 1:8 ratio (95%), for compound **VIIc** at 40°C and 1:5 ratio (47%), for compound **VIId** at 60°C and 1 : 4 ratio (39%), for compound **VIIe** at 65°C and 1 : 5 ratio (46%).

***N,N*′-Diacetyl-2,5-dichloro-1,4-phenylenediamine (IXa).** Through a solution of 0.5 g of compound **VIIIa** in 3 ml of DMF or of mixture DMF–acetic acid, 1 : 5, was passed chlorine gas at a rate 15–20 ml min^{-1} till the additional weight of the mixture corresponded to the desired molar ratio initial compound–chlorine, 1 : 2 or 1 : 3. The temperature was maintained in the 40–55°C range. To the end of chlorination separated colorless precipitate of the reaction product **IXa**. The product was recrystallized from DMF. The best yield of compound **IXa**, 64%, was obtained at chlorination in the DMF–acetic acid mixture, 1 : 5, at 45°C and molar ratio initial compound–chlorine 1 : 3.

***N,N*′-Diaroyl-2,5(2,6-,2,3-)dichloro-1,4-phenylenediamines (IXb–e, Xb–e, XIb–e).** The chlorination of compounds **VIIIb–e** was carried out as described above in DMF or in the mixture DMF–acetic acid, 1 : 5, at 25–50°C and molar ratios initial product– chlorine in the range from 1 : 2 to 1 : 6. The colorless reaction products consisting of isomer mixtures **IX, X, XI** precipitated to the end of chlorination and were recrystallized from DMF. The best yield of the isomer mixtures was obtained at chlorination in the DMF–acetic acid mixture, 1 : 5, at 40°C and molar ratio initial compound–chlorine 1 : 5. The yields of the chlorination products were as follows: **IXb, Xb, XIb** 51%, **IXc, Xc, XIc** 52%, **IXd, Xd, XId** 61%, **IXe, Xe, XIe** 58%.

***N,N*′-Diaroyl-2,5(2,6-,2,3-)dichloro-1,4-benzoquinone diimines (XIIb–e, XIIIb–e, XIVb–e)** were prepared by oxidation of isomer mixtures **IXb–e, Xb–e, XIb–e** with lead tetraacetate in benzene along procedure described in [2]. The reaction products were recrystallized from heptane. The content of isomers in the mixtures was determined from the corresponding signals on the integration curves in the ^1H NMR spectra. According to elemental analyses in the isomer mixtures are no substances of the other composition.

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