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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Effect of Structural Factors and Solvent Nature in Bromination of Anilines

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Abstract—Reaction of electrophilic bromination of aniline containing various ortho, meta, and para substituents in the aromatic ring was studied. The optimal conditions for synthesis of mono-, di-, tri-, and tetrabromo derivatives of aniline and brominated analog of Aniline Black were found.

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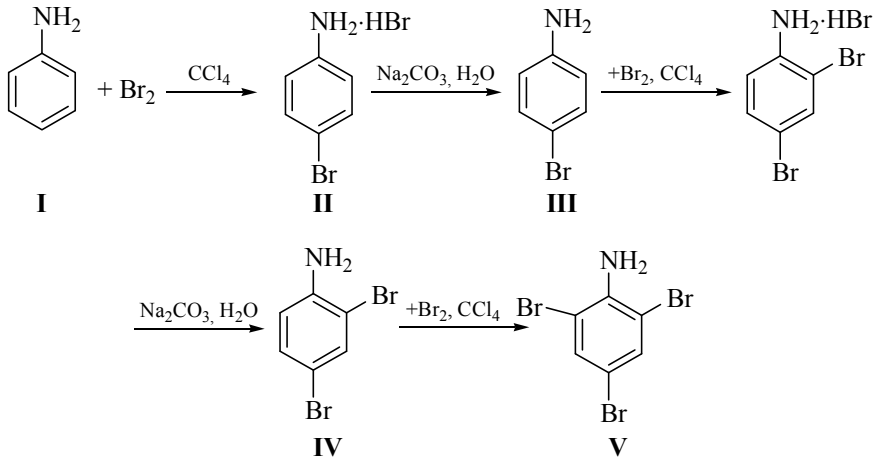
An analysis of numerous publications devoted to bromination of anilines [1–7] demonstrated that studies in this field were insufficient in view of the fact that the products of the synthesis of brominated anilines served as efficient fire-retardants [8], biologically active substances [9], pharmaceutical preparations [10], and herbicides [11].

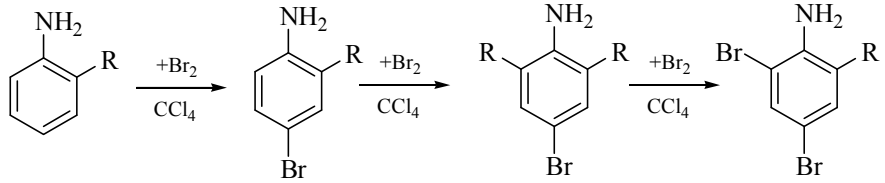
The conjugation of the lone pair of electrons of a nitrogen atom with the π-system of the aromatic ring (*p*,π conjugation) [12] and changes in the basicity of aniline, depending on the nature and position of substituents in the phenyl ring make it possible to develop an effective technology for the synthesis of brominated aromatic amino compounds and their derivatives. In this context, it is of interest to study specific features of the behavior of *o-*, *m-*, and *p*-substituted anilines in the bromination reaction [13–15].

It is known that, in reactions of electrophilic bromination of aromatic amino compounds (e.g., aniline) by molecular bromine in the presence of an organic solvent (CCl_4), the evolving hydrogen bromide converts a free amino group to the protonated form NH_3^+ [16]. The deactivating effect of the ammonium cation results in that the π-electron density of the aromatic ring decreases and monobromoaniline is formed as a quaternary salt (**II**) whose treatment with a weak aqueous solution of soda yields pure monobromoaniline (**III**). Similarly, di- (**IV**) and tribromo- (**V**) anilines are obtained:



Tetra- and pentabromo derivatives cannot be obtained because the steric factor hinders further addition of bulky bromine atoms at the *o*-position with respect to the already present bromine atom. In bromination of **I** in an aqueous medium, the evolving hydrogen bromide has not enough time to convert the product obtained to salt **II**, because the latter is readily hydrolyzed. In this case, bromine atoms in the aromatic ring activate further substitution, and, therefore, bromination of aniline by molecular bromine in an aqueous medium with a mixture HBr + H_2O_2 yields tribromoaniline **V**. This means that hydrolysis of quaternary salts restores the conjugation of the 2*p*-orbital of nitrogen with π-orbitals of the phenyl ring.

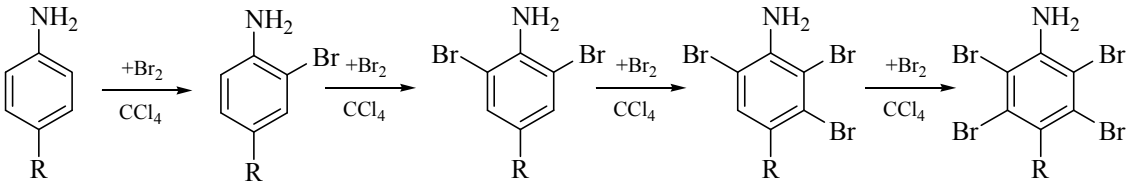
Depending on the electronic nature and position of substituents (*o-, m-, p*-positions), anilines behave differently in bromination in organic and aqueous media. In bromination in a nonpolar organic solvent (CCl_4), *o*-substituted anilines form products of monobromo substitution, **XI–XV**, and in further bromination, disubstituted anilines **XVI–XX**. As for the tribromo derivatives of anilines, **XXI–XXIII**, they are only obtained in bromination of *o*-substituted anilines with electron-donor substituents, **VI–VIII**, in CCl_4. In these conditions, only two hydrogen atoms of the benzene ring are substituted in anilines containing electron-acceptor substituents, **IX** and **X**, which yields dibromo derivatives **XIX** and **XX**:



VI–X **XI–XV** **XVI–XX** **XXI–XXIII**

R = CH_3 (**VI**, **XI**, **XVI, XXI**); OH (**VII, XII, XVII, XXII**); Cl (**VIII, XIII, XVIII, XXIII**); NO_2 (**IX, XIV, XIX**); COOH (**X, XV, XX**).

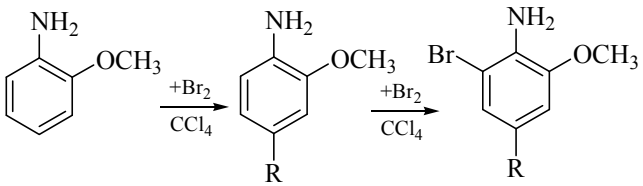
p-Substituted anilines **XXIV–XXVIII** with such substituents behave similarly and form, in stages, mono- (**XXXI–XXXV**), 2,6-di- (**XXXVI–XL**), 2,6-tri- (**XLI–XLIII**), and 2,3,5,6-tetrabromo derivatives (**XLIV–XLVI**) of aniline in the case of electron-donor substituents, and mono- (**XXXI–XXXV**) and dibromo derivatives (**XXXVI–XL**) for compounds with electron-acceptor substituents:



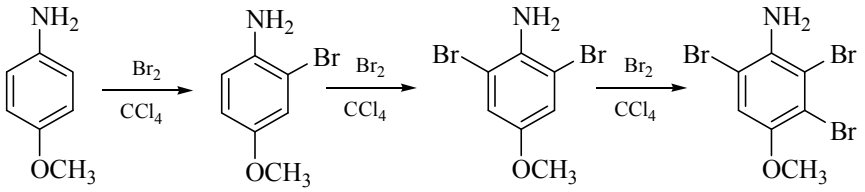
XXIV–XXVII **XXXI–XXXV** **XXXVI–XL** **XLI–XLII** **XLIV–XLVI**

R = CH_3 (**XXIV, XXXI, XXXVI, XLI, XLIV**); OH (**XXV, XXXII, XXXVII, XLII, XLV**); Cl (**XXVI, XXXIII, XXXVIII, XLIII, XLVI**); NO_2 (**XXVII, XXXIV, XXXIX**); COOH (**XXVIII, XXXV, XL**).

If a methoxy group is the substituent, the nature of bromination product formed in CCl_4 depends on its position in the aromatic ring: at the *o*-position, the bromination products are monobromo- and 4,6-dibromo derivatives **XLVII** and **XLVIII**; at the *p*-position, these are monobromo- (**XLIX**), 2,6-dibromo- (**L**), and 2,3,6-tribromo- (**LI**) derivatives of aniline. This is apparently due to the steric influence of the methoxy group, which blocks one of the *o*-positions of the aromatic ring. In the case of the *o*-OCH_3 compound **XXIX**, position 3 is blocked by the methoxy group, and position 5, by two bulky bromine atoms; for *p*-OCH_3 (**XXX**), only one of the *o*-positions with respect to the OCH_3 group is blocked, which results in mono- (**XLIX**), di- (**L**), and then 2,3,6-tribromo-4-methoxyaniline (**LI**) formed:



XXIX **XLVII** **XLVIII**

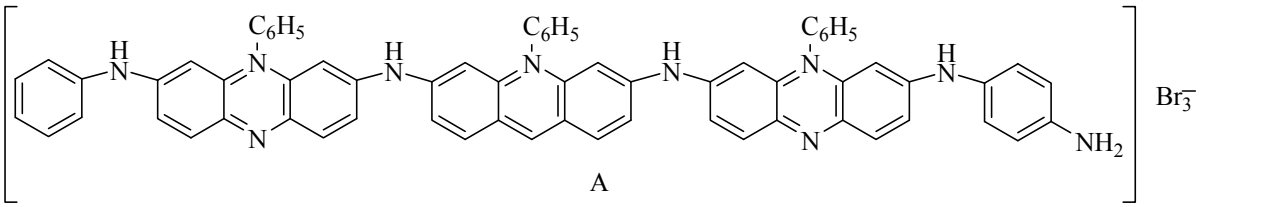


XXX **XLIX** **L** **LI**

The reaction of bromination of anilines with *o*- and *p*-substituents of the first kind in an aqueous medium yields a black solid product of complex composition. According to an elemental analysis and results of molecular mass determination, this substance is a brominated analog of Aniline Black [17]:

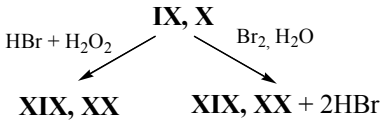
VI–VIII $\xrightarrow{+Br_2}$ Brominated analog of Aniline Black $\xleftarrow{+Br_2}$ **XXIV–XXVI**.

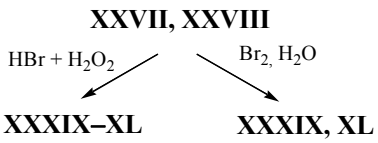
The elemental composition of Aniline Black (A) corresponds to the empirical formula $(C_6H_5N)_x$, its intensive reduction yields 4,4'-diaminodiphenylamine. On the basis of these data, the structure of brominated Aniline Black can be represented as



A

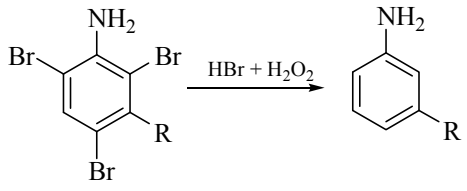
Under similar conditions, *o*- and *p*-substituted anilines with substituents of the second kind are brominated without oligomerization and blackening of the reaction mass. Apparently, the key role is played in these processes by the negative inductive effect of the substituent, which leads to 4,6- and 2,6-dibromoanilines, respectively:



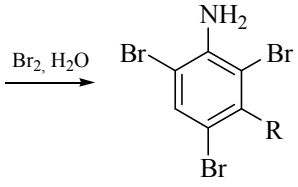


These facts confirm the decisive role of the electronic nature of substituents in the stabilization of localized or delocalized form of the aromatic ring in the bromination process.

As for *m*-substituted anilines **LII–LVI**, their bromination and oxybromination always lead, irrespective of the nature of a substituent, to the corresponding 2,4,6-tribromoanilines **LVII–LXI** [18]:



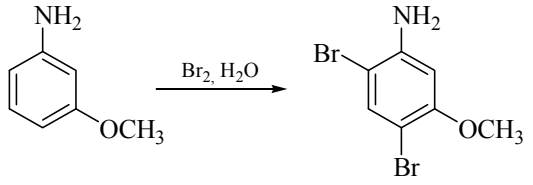
LVII–LXI **LII–LVI**



LVII–LXI

R = CH_3 (**LII, LVII**); OH (**LIII, LVIII**); Cl (**LIV, LIX**); NO_2 (**LV, LX**;); COOH (**LVI, LXI**).

The mesomeric effect of a substituent in the m-position is nearly zero because *m*-quinoid boundary structures are energetically unfavorable. Therefore, the amino group is not activated by a substituent of the second kind and hydrogen in positions 2, 4, and 6 at the aromatic ring is readily substituted. The bromination of *m*-azinidine yields 4,6-dibromo-3-methoxyaniline, which confirms the superior role of the steric effect over the inductive and mesomeric influences:



LXII **LXIII**

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Tesla BS-487 spectrometer (working frequency 80 MHz) in $CDCl_3$, with HMDS as internal standard [19]; IR spectra were obtained with a UR-20 instrument in the spectral range 400–3800 cm–1 for suspensions in mineral oil [20]; UV spectra were recorded on a Specord M-40 spectrophotometer in the spectral range 180–400 nm for solutions in ethanol (concentration 10^{-4} M, 1-cm-thick cell) [21].

The purity of the compounds synthesized was verified by TLC, with L 5/40 μ silica gel as sorbent [22] and spot visualization by UV light.

The *o-, m-*, and *p*-substituted anilines used in the study were of reagent purity.

General procedure for synthesis of monobromoanilines. To a solution of 0.1 mol of a substituted aniline **I, VI–X, XXIV–XXVIII** in 200 ml of CCl_4 was added dropwise, under vigorous agitation and cooling with ice, in the course of 3 h 0.1 mol of Br_2 in 100 ml of CCl_4 , with the temperature of the mixture maintained at 10°C. After the whole amount of Br_2 was added, the mixture was kept at room temperature for additional 1 h and the precipitate

Table 1. Selected physicochemical parameters and elemental composition of mono- and dibromo derivatives of anilines

Comp. no.	R	Yield, %	mp, °C	R_f	Found, %					Formula
					C	H	N	Br	Cl	
III	H	94	66–66.5	0.67	42.19	3.50	8.19	45.86		C_6H_6BrN
XI	*o*-CH_3	95	59	0.76	45.31	4.28	7.63	43.19		C_7H_8BrN
XII	*o*-OH	96	162	0.80	38.03	2.97	7.40	41.88		C_6H_6BrNO
XIII	*o*-Cl	95	70	0.73	34.62	2.51	6.65	38.81	17.22	C_6H_5BrClN
XIV	*o*-NO_2	98	18	0.80	32.79	2.37	13.11	37.00		$C_6H_5BrN_2O_2$
XV	*o*-COOH	98	220	0.77	39.12	2.62	6.97	37.11		$C_7H_6BrNO_2$
XXXI	*p*-CH_3	97	36	0.76	45.31	4.27	7.48	42.96		C_7H_8BrN
XXXII	*p*-OH	93	148	0.83	37.81	3.02	7.11	42.14		C_6H_6BrNO
XXXIII	*p*-Cl	95	69	0.70	34.50	2.52	6.90	38.29	17.27	C_6H_5BrClN
XXXIV	*p*-NO_2	94	104	0.78	32.75	2.81	1.13	36.59		$C_6H_5BrN_2O_2$
XXXV	*p*-COOH	99	204	0.81	38.81	2.84	6.91	38.00		$C_7H_6BrNO_2$
XLVII	*o*-OCH_3	97	60	0.79	41.23	4.03	6.77	40.17		C_7H_8BrNO
XLIX	*p*-OCH_3	98	64	0.71	41.93	3.67	6.72	40.09		C_7H_8BrNO
IV	H	99	79	0.63	28.69	2.01	5.58	63.74		$C_6H_5Br_2N$
XVI	*o*-CH_3	93	50	0.57	30.94	2.45	5.11	61.02		$C_7H_7Br_2N$
XVII	*o*-OH	95	145	0.73	26.06	1.80	5.24	60.11		$C_6H_5Br_2NO$
XVIII	*o*-Cl	94	95	0.67	25.24	1.49	4.76	56.55	11.94	$C_6H_4Br_2Cl$
XIX	*o*-NO_2	96	126	0.68	24.19	1.27	9.40	53.79		$C_6H_4Br_2N_2O_2$
XX	*o*-COOH	98	235	0.73	28.37	1.57	4.14	54.16		$C_7H_5Br_2NO_2$
XXXVI	*p*-CH_3	89	74–5	0.61	31.14	2.33	5.07	60.47		$C_7H_7Br_2N$
XXXVII	*p*-OH	91	157	0.71	26.90	1.76	5.17	60.81		$C_6H_5Br_2NO$
XXXVIII	*p*-Cl	94	93	0.57	25.14	1.31	4.63	55.87	12.51	$C_6H_4Br_2Cl$
XXXIX	*p*-NO_2	87	197	0.70	24.27	1.41	9.38	53.76		$C_6H_4Br_2N_2O_2$
XL	*p*-COOH	93	св. 290	0.76	28.19	1.71	4.26	54.21		$C_7H_5Br_2NO_2$
XLVIII	*o*-OCH_3	90	86	0.58	29.01	2.39	5.03	57.14		$C_7H_7Br_2NO$
XLIX	*p*-OCH_3	93	81	0.62	29.42	2.23	4.76	57.22		$C_6H_4Br_2NO$
LXIII	*m*-OCH_3	90	136	0.52	29.63	2.51	4.57	56.83		$C_7H_7Br_2NO$

Table 1. (Contd.)

Comp. no.	Calculated, %				
	C	H	N	Br	Cl
III	41.89	3.52	8.14	46.45	
XI	45.19	4.33	7.53	42.95	
XII	38.33	3.22	7.45	42.50	
XIII	34.90	2.44	6.78	38.70	17.17
XIV	33.21	2.32	12.91	36.82	
XV	38.92	2.80	6.48	36.99	
XXXI	45.19	4.33	7.53	42.95	
XXXII	38.33	3.22	7.45	42.50	
XXXIII	34.90	2.44	6.78	38.70	17.17
XXXIV	33.21	2.32	12.91	36.82	
XXXV	38.92	2.80	6.48	36.99	
XLVII	41.61	3.99	6.93	39.55	
XLIX	41.61	3.99	6.93	39.55	
IV	28.72	2.01	5.58	63.69	
XVI	31.73	2.66	5.29	60.32	
XVII	27.00	1.89	5.25	59.87	
XVIII	25.25	1.41	4.91	56.00	12.42
XIX	24.35	1.36	9.47	54.00	
XX	28.51	1.71	4.75	54.19	
XXXVI	31.73	2.66	5.29	60.32	
XXXVII	27.00	1.89	5.25	59.87	
XXXVIII	25.25	1.41	4.91	56.00	12.42
XXXIX	24.35	1.36	9.47	54.00	
XL	28.51	1.71	4.75	54.19	
XLVIII	29.93	2.51	4.99	56.88	
XLIX	29.93	2.51	4.99	56.88	
LXIII	29.93	2.51	4.99	56.88	

formed was filtered off, washed with distilled water to remove the quaternary salt, and dried. The resulting crystalline product was treated with a weak aqueous solution of K_2CO_3, filtered off on a Schott filter, several times washed with distilled water, dried, and analyzed. The yield of monobromo derivatives of aniline was 93–98%. Selected physicochemical parameters of these compounds are listed in Table 1.

General procedure for synthesis of dibromoanilines. To a solution of 0.1 mol of monobromoaniline in 200 ml of CCl_4 was added, under vigorous agitation and cooling with ice, 0.1 mol of Br_2 in 100 ml of CCl_4 . The supply of bromine was adjusted so that no yellowish-brownish precipitate was formed and the temperature of the reaction mass did not exceed 20–25°C. Then the reaction mass was kept at room temperature for additional 1 h and the solid precipitate was filtered off, several times washed with distilled water, and dried. The yield of dibromoanilines was 87–98%. Selected physicochemical parameters of these compounds are listed in Table 1.

Tribromoanilines. *a*. To a solution of 0.1 mol of dibromoaniline in 200 ml of CCl_4 was added, under vigorous agitation, 0.1 mol of Br_2 in 100 ml of CCl_4 , with the temperature of the mixture maintained at 30–40°C. After the whole amount of bromine was added, the reaction mass was kept at room temperature for 1 h, the precipitate formed was filtered off, several

Table 2. Selected physicochemical parameters and elemental composition of tri- and tetrabromo derivatives of anilines

Comp. no.	R	Yield, %	mp, °C	R_f	Found, %					Formula
					C	H	N	Br	Cl	
V	H	99	119	0.65	21.81	1.24	4.24	71.76		$C_6H_4Br_3N$
XXI	*o*-CH_3	94	48	0.55	24.19	1.53	3.88	69.41		$C_7H_6Br_3N$
XXII	*o*-OH	92	139	0.68	20.69	1.05	3.89	69.11		$C_6H_4Br_3NO$
XXIII	*o*-Cl	91	92	0.54	19.48	0.80	3.65	65.44	9.37	$C_6H_3Br_3ClN$
XLI	*p*-CH_3	94	69	0.59	24.12	1.42	3.31	69.93		$C_7H_6Br_3N$
XLII	*p*-OH	95	94	0.69	20.63	0.94	3.86	69.26		$C_6H_4Br_3NO$
XLIII	*p*-Cl	92	87	0.56	19.47	0.77	3.61	65.82	9.66	$C_6H_3Br_3ClN$
LI	*p*-OCH_3	85	76	0.63	22.81	1.53	3.87	66.01		$C_7H_6Br_3NO$
LVII	*m*-CH_3	89	97	0.56	24.26	1.46	4.00	70.93		$C_7H_6Br_3N$
LVIII	*m*-OH	94	119	0.52	20.43	1.05	4.12	69.13		$C_6H_4Br_3NO$
LIX	*m*-Cl	91	123	0.51	19.62	0.91	3.76	65.62	10.01	$C_6H_3Br_3ClN$
LX	*m*-NO_2	90	102	0.69	19.03	0.78	7.33	63.90		$C_6H_3Br_3N_2O_2$
LXI	*m*-COOH	97	170	0.71	29.31	1.14	3.67	64.47		$C_7H_4Br_3NO_2$
XLIV	*p*-CH_3	92	66	0.55	19.72	0.89	3.12	75.01		$C_7H_5Br_4N$
XLV	*p*-OH	85	65	0.69	16.78	0.70	2.92	74.99		$C_6H_3Br_4NO$
XLVI	*p*-Cl	93	73	0.54	15.99	0.39	3.10	72.11	7.98	$C_6H_2Br_4ClN$

Table 2. (Contd.)

Comp. no.	Calculated, %				
	C	H	N	Br	Cl
V	21.85	1.22	4.25	72.68	
XXI	24.45	1.76	4.07	69.72	
XXII	20.84	1.17	4.05	69.32	
XXIII	19.78	0.83	3.85	65.81	9.73
XLI	24.45	1.76	4.07	69.72	
XLII	20.84	1.17	4.05	69.32	
XLIII	19.78	0.83	3.85	65.81	9.73
LI	23.36	1.68	3.89	66.62	
LVII	24.45	1.76	4.07	69.72	
LVIII	20.84	1.17	4.05	69.32	
LIX	19.78	0.83	3.85	65.81	9.73
LX	19.23	0.81	7.47	63.96	
LXI	22.49	1.08	3.75	64.12	
XLIV	19.89	1.19	3.31	75.61	
XLV	16.97	0.71	3.30	75.25	
XLVI	16.26	0.45	3.16	72.12	8.01

times washed with distilled water, and dried. The yield of tribromoanilines was 85–99%. Selected physicochemical parameters of these compounds are listed in Table 2.

b. Into a solution of 0.1 mol of a substituted aniline in 250 ml of 25% HBr was added in the course of 3 h, under vigorous agitation, 30.54 ml of a 30% H_2O_2 solution, with the temperature of the mixture maintained at around 10°C (cooling with ice). The resulting crystalline product was filtered off, several times washed with distilled water, and dried in air. Parameters of the compounds obtained **V, XXI–XXIII, XLI –XLIII, LI,** and **LVII–LXI** are listed in Table 2.

Tetrabromoanilines. To a solution of 0.1 mol of a tribromoaniline, **XLI –XLIII**, in 250 ml of CCl_4 was added, under vigorous agitation, 0.1 mol of Br_2 in 50 ml of CCl_4. After the whole amount of bromine was consumed, the reaction mixture was kept at room temperature for additional 1 h and the solid product was filtered off, several times washed with distilled water, and dried. The yield of tetrabromoanilines **XLIV**–**XLVI** was 85–93%; their characteristics are listed in Table 2.

CONCLUSIONS

(1) Bromination of substituted anilines in nonpolar solvents leads, irrespective of the nature of a substituent, to tetrabromo derivatives via formation of mono-, di-, and tribromo derivatives.

(2) The result of bromination in an aqueous medium depends both on the nature of a substituent and on its position in the aromatic ring. Presence of electron-donor substituents in *o*- and *p*-positions leads to formation of Aniline Black, whereas electron-acceptor substituents yield mono-, di-, tri-, and tetrabromo derivatives. *m*-Substituted anilines form, irrespective of the properties of a substituent, 2,4,6-tribromoanilines.

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