

# Induced Bromination of Aromatic Hydrocarbons by Alkali Metals Bromides and Sodium Hypochlorite

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**Abstract**—Induced bromination of aromatic compounds in a system MBr–acid–NaOCl was studied. Optimum conditions of the process were developed, kinetics of the reactions were investigated, and the process mechanism was suggested. The bromination occurs both with the bromine *in statu nascendi* and with the hypobromous acid by hydrogen substitution exclusively in the aromatic ring.

The bromine introduction into an aromatic ring is one of the most important organic reactions widely used both in laboratory and in industry. Bromine-substituted aromatic hydrocarbons are applied as key compounds to the synthesis of drugs [1], specialty epoxy resins, flame-retardants, flame-resistant polymer materials [2–4]. The halogenation is performed mainly by two procedures: by direct halogenation with free halogens, and by substitution with the use of halogen-containing reagents. The vast majority of recent publications deals with the arene bromination with the molecular bromine [5], chlorine–bromine mixtures [6], with bromine in the presence of zeolites [7, 8], potassium bromate in the 65% H<sub>2</sub>SO<sub>4</sub> [9, 10], KBr and H<sub>2</sub>O<sub>2</sub> in acetic acid in the presence of NaBO<sub>3</sub>·4H<sub>2</sub>O or (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O [11], and zeolite H-ZSM-5 [12], with hydrobromic acid with an oxidant sulfoxide (Me<sub>2</sub>SO) [13], H<sub>2</sub>O<sub>2</sub> [14, 15], or *tert*-butyl hydroperoxide [16], with *N*-bromosuccinimide [17–19], and with other bromine-containing reagents [20].

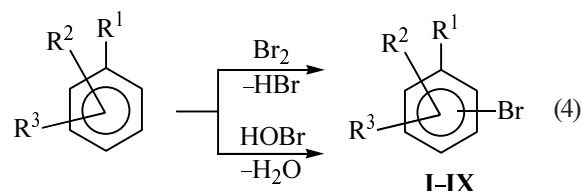
The alternative methods of the oxidative halogenation of aromatic compounds were treated in detail in review [21].

We showed formerly that the bromination of aromatic compounds [22, 23] and polystyrene [24] might be carried out in water solutions of alkali metals bromides involving various oxidants. No published information exists on the induction of arene bromination in a system MBr–HX–NaOCl.

This study was performed with a goal to reveal the regular trends in the induced bromination of benzene and its derivatives in the system NaBr(KBr)–HX–NaOCl employed as a brominating agent.

† Deceased.

The reaction of induced bromination proceeds in succession through stages (1–4).



R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H (I); R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = CH<sub>3</sub> (II), C<sub>2</sub>H<sub>5</sub> (III), *i*-C<sub>3</sub>H<sub>7</sub> (IV), C<sub>2</sub>H<sub>5</sub>O (VIII); R<sup>1</sup> = H, R<sup>2</sup> = R<sup>3</sup> = CH<sub>3</sub> (1, 2) (V), (1, 3) (VI), (1, 4) (VII); R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = CH<sub>3</sub> (1, 2, 4) (IX); X = Cl<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, RSO<sub>3</sub><sup>-</sup>.

The yield of brominated products and the bromination selectivity depended on the molar ratio of the reagents, on the temperature and time of the process. With the temperature growing from 293 to 323 K the yield of the monobromobenzene and monobromoalkylbenzenes increased from 54.3 to 98.6 wt % (Table 1). Note that in going from toluene to isopropylbenzene at the growing bulk of the alkyl group a partial dealkylation takes place affording bromobenzene. As seen from Table 1, no bromobenzene formed from toluene, but in the case of ethylbenzene or isopropylbenzene the yield of the bromobenzene reached 6.5 wt %. In the induced bromination of di- and trisubstituted alkylbenzenes the yield of the corresponding monobromo derivatives increases (from 85.8 to 98.8 wt % respectively).

**Table 1.** Effect of temperature on the yield of bromoaromatic compounds (ArH:NaBr:NaOCl = 1:2:1, reaction time 480 min)

Initial compounds	Reaction product no.	Yield, wt%			
		293 K	303 K	313 K	323 K
C <sub>6</sub> H <sub>6</sub>	<b>I</b>	54.3	62.8	69.2	76.6
CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	<b>IIa</b> (2) <sup>a</sup>	23.5	27.8	32.6	40.2
	<b>IIb</b> (4)	60.3	70.6	66.3	58.4
C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	<b>IIIa</b> (2)	16.2	25.3	26.0	27.2
	<b>IIIb</b> (4)	63.5	65.8	68.6	68.0
	<b>I</b> <sup>b</sup>	2.3	3.2	3.6	3.6
iso-C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>5</sub>	<b>IVa</b> (2)	4.8	7.2	11.6	12.8
	<b>IVb</b> (4)	67.2	78.0	76.5	75.6
	<b>I</b> <sup>b</sup>	2.6	6.2	6.3	6.5
1,2-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>Va</b> (3)	19.2	24.6	26.8	28.5
	<b>Vb</b> (4)	66.5	68.5	67.9	67.6
1,3-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>VI</b> (4)	89.8	95.4	97.6	98.9
1,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>VII</b> (2)	83.6	92.5	94.7	96.8
C <sub>2</sub> H <sub>5</sub> OC <sub>6</sub> H <sub>5</sub>	<b>VIIIa</b> (2)	10.5	13.5	14.2	14.8
	<b>VIIIb</b> (4)	67.8	78.6	80.4	81.5
1,2,4-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	<b>IX</b> (5)	91.5	96.2	98.8	–

The increase in the amount of salt (NaBr or KBr) to the ratio of 2.0 mol per 1 mol of arene did not considerably affect the yield and the selectivity of the reaction product formation. However the use of excess aromatic compound results in a significant growth of the yield of monobromo derivative.

The data in Table 2 show that at increase of ethylbenzene and isopropylbenzene quantity from 1.0 to 4.0 mol the growing bromobenzene formation is also observed like in the direct bromination of *tert*-butylbenzene [27] and in chlorination of 4-*tert*-butyltoluene [26].

The selectivity of reactions and isomeric composition of the arising bromo derivatives to a significant degree depends on the nature of the alkyl substituents. During induced bromination of methyl-, ethyl-, and ethoxybenzene at 293 K the content of the *para*-isomer in the product obtained was respectively 2.6, 3.9, and 6.5 times more than that of the *ortho*-isomer. The bulky *iso*-C<sub>3</sub>H<sub>7</sub> group even more hampers hydrogen substitution in the *ortho*-position: The content of the *ortho*-isomer in

**Table 2.** Dependence of composition of monobromo derivatives on the molar ratio of ethyl- and isopropylbenzene (temperature 293 K, reaction time 300 min, NaBr–NaOCl, 1:1)

C <sub>6</sub> H <sub>5</sub> R, <sup>a</sup> mol	Composition according to GLC, wt%				Yield of monobromo derivatives on used NaOCl, wt% <sup>c</sup>
	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> <i>iso</i> - C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> Br <i>iso</i> -C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> Br		C <sub>6</sub> H <sub>5</sub> Br <sup>b</sup>	
		<i>ortho</i> - isomer	<i>para</i> - isomer		
1	34.6	11.6	52.6	1.2	65.4
	43.7	4.3	48.2	3.8	56.3
2	64.2	3.5	20.4	11.9	35.8
	60.4	2.2	22.6	14.8	39.6
3	68.5	1.2	13.5	16.8	31.5
	67.3	1.6	12.5	19.6	33.7
4	72.0	0.8	5.8	21.5	28.1
	71.4	0.6	5.3	22.7	28.6

<sup>a</sup>R = C<sub>2</sub>H<sub>5</sub> and *iso*-C<sub>3</sub>H<sub>7</sub>.

<sup>b</sup>Upper line corresponds to the yield of monobromobenzene from ethylbenzene, bottom line is the same for isopropylbenzene.

<sup>c</sup>Upper line corresponds to the yield of bromination products from ethylbenzene, bottom line is the same for isopropylbenzene.

the bromides mixture is 14 times less than that of the *para*-isomer. In the bromination of 1,2-dimethylbenzene the amount of 4-bromo-1,2-dimethylbenzene 3.5 times exceeds the amount of 3-bromo-1,2-dimethylbenzene.

We established applying the chromatographic analysis and IR and <sup>1</sup>H NMR spectrometry [27, 28] that relative content of one or another isomer in the reaction products depended on the nature of the substituents in the aromatic ring. In the IR spectra of monobromo derivatives absorption bands appear in the region 748, 805, and 810 cm<sup>-1</sup> characteristic of 1,2- and 1,4-substituted benzene rings. The bands at 752–826 cm<sup>-1</sup> belong to the out-of-plane vibration of the C–Br bond in the molecules of the monobromo derivatives of methyl-, ethyl-, isopropyl-, and ethoxybenzene [28].

The <sup>1</sup>H NMR spectra of compounds obtained lacked proton signals in the 4.0 ppm region evidencing that the induced bromination of the mentioned alkylarenes occurred at the cost of the protons at the aromatic ring. In particular, the proton signals from the CH<sub>3</sub> group of the monobromotoluene located in position 2 with respect to the bromine atom appeared at 2.2 ppm, and the corresponding peak from position 4 at 2.08 ppm.

The degenerate multiplet in the region 6.8–7.3 ppm corresponded to the four protons of the aromatic ring [27]. In the <sup>1</sup>H NMR spectrum of the monobromoethylbenzene in the upfield region appear two triplets with the

chemical shifts 1.15 and 1.12 ppm belonging to the protons of two CH<sub>3</sub> groups, and two quartets at 2.70 and 2.50 ppm from two CH<sub>2</sub> groups of the ethyl substituents located in positions 2 and 4 with respect to bromine. In the <sup>1</sup>H NMR spectrum of monobromoisopropylbenzene two doublets with a coupling constant *J* 7 Hz of CH<sub>3</sub> groups are observed in the upfield region (0.87 and 1.35 ppm). The two sextets belonging to the methine protons of the isopropyl substituent with the same coupling constants appear at 2.75 and 3.35 ppm for the *ortho*- and *para*-isomer respectively. In the region 6.9 and 7.3 ppm the degenerate multiplet of aromatic protons is observed common for both isomers.

In the IR spectrum of the monobromo-substituted *o*-xylene were registered absorption bands in the region 776, 810, and 864 cm<sup>-1</sup> characteristic of 1,2,3- and 1,2,4-trisubstituted aromatic ring [28]. The formation of two isomers is confirmed also by the <sup>1</sup>H NMR spectra where proton signals appear from methyl groups in positions 2 and 3 with respect to bromine in the region 2.09 and 2.15 ppm for 3-bromo-1,2-dimethylbenzene and 2.15 ppm for 4-bromo-1,2-dimethylbenzene. The analysis of IR spectra corresponding to the monobromo-substituted *m*- and *p*-xylenes showed that the absorption bands in the regions 810 and 876 cm<sup>-1</sup> belong respectively to aromatic rings trisubstituted in positions 1, 3, 4 and 1, 2, 4.

In the <sup>1</sup>H NMR spectrum of 4-bromo-1,3-dimethylbenzene two singlets of the methyl groups in positions 2 and 4 with respect to bromine are observed upfield at 2.05 and 2.18 ppm. Two protons of the aromatic ring with the chemical shifts 6.6 and 7.15 ppm (H<sup>5</sup> and H<sup>6</sup>) appear as an *AB* system (*J* 8 Hz); therewith the doublet of H<sup>6</sup> located in position 3 with respect to bromine is observed in the stronger field at 6.9 ppm as should be expected. Methyls in the molecule of 2-bromo-1,4-dimethylbenzene situated in positions 2 and 3 with respect to bromine give rise to two singlets at 2.15 and 2.2 ppm.

To evaluate the effect of the alkyl group character on the reactivity we estimated the initial reaction rates at various temperatures and the values of activation parameters for the process of induced bromination of alkylbenzenes (Table 3).

As seen from Table 3, in the molecules of CH<sub>3</sub>-, C<sub>2</sub>H<sub>5</sub>-, C<sub>2</sub>H<sub>5</sub>O-, *iso*-C<sub>3</sub>H<sub>7</sub>-benzene position 4 is more reactive than position 2, and in the 1,2-dimethylbenzene the reactivity of position 4 is higher than that of position 3. The rate of formation of bromoarenes declines in the following order: 2-Br-1,4-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> > 4-Br-1,3-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> > 4-Br-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> ≈ 4-Br-C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>H<sub>5</sub> >

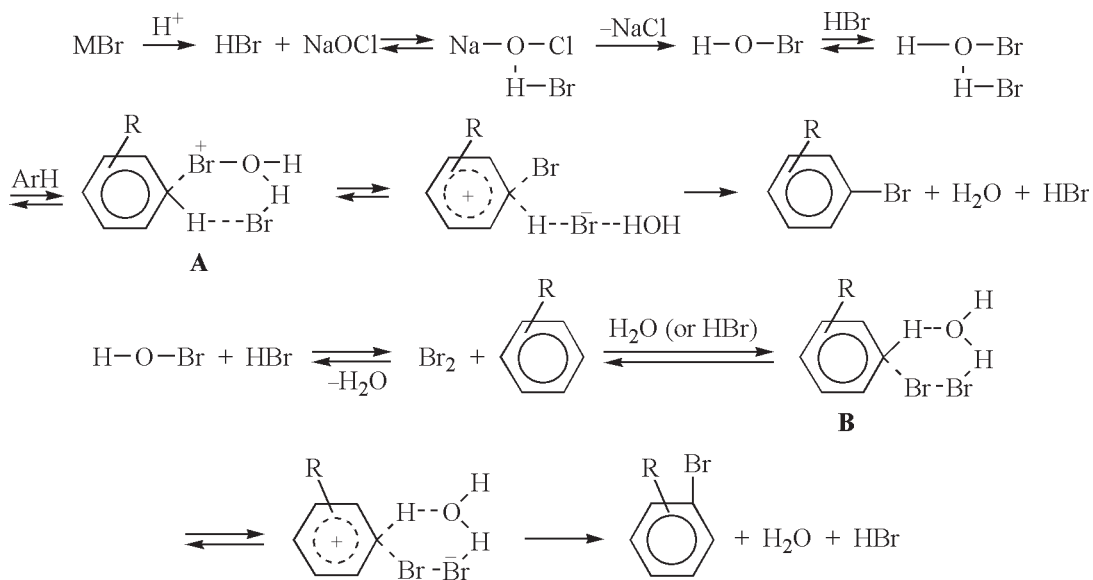
**Table 3.** Reaction rate and activation parameters of induced bromination of aromatic compounds

No. of bromo-derivative	$W \times 10^3$ , mol l <sup>-1</sup> min <sup>-1</sup> (303 K)	$E$ , kJ/mol	$\Delta H^\ddagger$ , kJ/mol	$-\Delta S^\ddagger$ , J/ (mol deg)	$\Delta G^\ddagger$ , kJ/mol
<b>I</b>	4.313	43.9	43.2	82.3	78.1
<b>IIa</b>	1.572	34.6	34.0	73.4	56.6
<b>IIb</b>	5.8	38.3	37.7	77.4	61.2
<b>IIIa</b>	1.104	29.5	28.9	69.0	48.9
<b>IIIb</b>	5.724	40.8	40.2	75.4	63.0
<b>IVa</b>	0.4965	25.1	24.5	64.4	44.6
<b>IVb</b>	5.043	30.8	30.1	65.2	49.8
<b>Va</b>	1.498	33.9	33.3	73.9	55.7
<b>Vb</b>	5.47	37.7	37.1	77.6	60.6
<b>VI</b>	7.273	50.3	49.7	85.4	75.6
<b>VII</b>	8.931	39.6	39.0	75.2	61.7
<b>VIIIa</b>	0.786	40.8	40.2	69.9	61.8
<b>VIIIb</b>	5.503	39.6	39.0	76.1	62.1

4-Br-C<sub>6</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>5</sub> > 4-Br-1,2-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> > 4-Br-C<sub>6</sub>H<sub>4</sub>C<sub>3</sub>H<sub>7-iso</sub> > BrC<sub>6</sub>H<sub>5</sub> > 2-Br-C<sub>6</sub>H<sub>4</sub>C<sub>3</sub>H<sub>7</sub> > 3-Br-1,2-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> > 2-Br-C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>H<sub>5</sub> > 2-Br-C<sub>6</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>5</sub> > 2-Br-C<sub>6</sub>H<sub>4</sub>C<sub>3</sub>H<sub>7-iso</sub>.

The lower reactivity of *iso*-C<sub>3</sub>H<sub>7</sub>C<sub>6</sub>H<sub>5</sub> compared with C<sub>2</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub> reveals the negative influence of the steric effect on the reaction rate, since the values of the inductive effect for both group are equal ( $\sigma$  -0.151) [29]. However the absolute value of the purely sterical Palm constant for *iso*-C<sub>3</sub>H<sub>7</sub> ( $E_S$  -0.85) is 2.3 times larger than that of the ethyl group ( $E_S$  -0.37). The variation of the reactivity in the compounds under study is consistent with the estimated values of the activation parameters. Relatively small decrease in the  $\Delta S^\ddagger$  value for this reagents system compared with the direct catalytic chlorination of aromatic compounds [30] favors greater ordering of the structure of the transition state suggesting formation of six-membered complexes **A** and **B** which further transform into  $\sigma$ -complexes whose decomposition provides the reaction products. According to the results obtained and in keeping with the published data [31–33] we suggest the following mechanism of the induced bromination of arenas in the presence of NaBr or KBr and NaOCl.

Consequently, the induced substitution by halogen in the aromatic ring occurs involving both the free bromine and the hypobromous acid.



The regular trend in the change of the reactivity of the alkylaromatic compounds (Table 3) confirms that in this system the reaction rate is limited not by the stage providing  $\pi$ -complexes **A** and **B** but by the stage of formation of bromoaromatic products.

#### EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord-80,  $^1\text{H}$  NMR spectra were registered on a spectrometer Tesla BS-487B (80 MHz). The initial reaction rates were estimated by differential method from the kinetic curves of the target products accumulation at different temperatures [34].

**Induced bromination of arenes.** The experiments were carried out in glass reactor of standard type equipped with a reflux condenser, a system of reagents supply, and a magnetic stirrer. The reactor was placed into a bath with automatically controlled temperature. Into the reactor was charged a desired amount of the aromatic hydrocarbon and water solution of NaBr (or KBr). Then in succession was added dropwise a necessary amount of acid (HCl or  $\text{H}_2\text{SO}_4$ ) and an aqueous sodium hypochlorite (18.5 or 26% solution) containing 110–153 g-ion/l of active chlorine. On completion of the run the organic layer was separated from the acidic water phase, neutralized with diluted water solution of sodium carbonate, dried over anhydrous calcium chloride, and subjected to distillation. The reaction progress was monitored by GLC measuring amount of unreacted arene and the isomeric composition of obtained brominated products. The GLC analysis was performed on

a chromatograph LKhM-7A. The products of induced bromination of benzene, toluene, and xylenes were analysed using a column 3000×3 mm packed with Silichrom-2 impregnated with  $\text{CoCl}_2$  in amount of 10 wt%, oven temperature 150°C; products of induced bromination of ethyl-, isopropyl-, and ethoxybenzene were separated on a column 3000×3 mm, stationary phase 5% XE-60 on Chromaton N-AW-DMCS, oven temperature 140°C. The flow rate of carrier gas (helium) was 40 ml/min. The individual isomers of bromo derivatives of aromatic compounds were prepared by Sandmeyer's reaction when necessary [35].

**Bromobenzene (I).** Into the reactor was charged 15.5 g (0.15 mol) of NaBr or KBr and 10 g of  $\text{H}_2\text{O}$ , and then dropwise within 30 min was added 18.0 g (0.15 mol) of 33% hydrochloric acid, 7.8 g (0.1 mol) of benzene, and within 2 h 93.1 g (0.15 mol) of 18.5% water solution of sodium hypochlorite (with active chlorine content 110 g-ion/l). The reaction mixture was stirred for 4 h at 303 K. On completion of the reaction the organic layer was separated and dried over anhydrous calcium chloride. The distillation afforded 12.96 g (82%) of bromobenzene, bp 150°C,  $n_D^{20}$  1.5598,  $d_4^{20}$  1.50120 [36, 37].

The same results were obtained at the use of 26% water solution of sodium hypochlorite (with active chlorine content 153 g-ion/l).

**Bromination of toluene** was similarly performed charging 9.2 g (0.1 mol) of toluene. On completion of the reaction after standard workup we got 16.8 g (98%) of bromination products, bp 181–185°C,  $n_D^{20}$  1.5580,  $d_4^{20}$  1.3970 [36, 37]. According to GLC data the product



contained 70.6 wt% of 4-bromotoluene (**IIa**) and 27.1% of 2-bromotoluene (**IIb**). The remaining part of the product contained unidentified compounds. Identical results were obtained with KBr and 26% water solution of NaOCl as oxidant.

**Bromination of ethylbenzene** was carried out in the same way. From 10.6 g (0.1 mol) of ethylbenzene we obtained 18.0 g (96.8%) of bromination products, bp 187–201°C,  $n_D^{20}$  1.5448,  $d_4^{20}$  1.3983 [36, 37]. According to GLC the product contained 71.8 wt% of 4-bromoethylbenzene (**IIIa**), 25.3 wt% of 2-bromoethylbenzene (**IIIb**), and 3.2 wt% of bromobenzene.

**Bromination of isopropylbenzene** was similarly performed. From 12.0 g (0.1 mol) of isopropylbenzene we obtained 18.3 g (91.4%) of bromination product, bp 210–219°C,  $n_D^{20}$  1.5385,  $d_4^{20}$  1.2975 [36, 37]. According to GLC the product contained 78.0 wt% of 4-BrC<sub>6</sub>H<sub>4</sub>C<sub>3</sub>H<sub>7</sub>-*iso* (**IVa**), 7.2 wt% of 2-BrC<sub>6</sub>H<sub>4</sub>C<sub>3</sub>H<sub>7</sub>-*iso* (**IVb**), and 6.2 wt% of bromobenzene. The other substances were not identified. Identical results were obtained with KBr and 26% water solution of NaOCl as oxidant.

**Bromination of 1,2-dimethylbenzene** was similarly performed. From 10.6 g (0.1 mol) of 1,2-dimethylbenzene we obtained 17.4 g (93.5%) of bromination products, bp 212–216°C,  $n_D^{20}$  1.5560,  $d_4^{20}$  1.3723 [36, 37]. According to GLC the product contained 68.6 wt% of 4-Br-1,2-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**Va**) and 24.6 wt% of 3-Br-1,2-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**Vb**). Identical results were obtained with KBr and 26% water solution of NaOCl as oxidant.

**Bromination of 1,3- and 1,4-dimethylbenzene** was similarly performed. After standard workup and distillation we isolated 17.7 g (95.4%) of 4-Br-1,3-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**VI**), bp 208–210°C,  $n_D^{20}$  1.5442,  $d_4^{20}$  1.3757 [36, 37], and 17.2 g (92.5%) of 3-Br-1,4-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**VII**), bp 199–200°C,  $n_D^{20}$  1.5503,  $d_4^{20}$  1.3738 [36, 37]. Identical results were obtained with KBr and 26% water solution of NaOCl (containing 153 g-ion/l of active chlorine) as oxidant.

**Bromination of ethoxybenzene** was similarly performed. From 12.2 g (0.1 mol) ethoxybenzene after standard workup and distillation we isolated 19.4 (96.0%) of 4-bromoethoxybenzene (**VIII**), bp 233°C [36, 37].

**5-Bromo-1,2,4-trimethylbenzene (IX)** was obtained in the same way from 12 g (0.1 mol) of 1,2,4-trimethylbenzene. In the course of the reaction crystalline substance separated that was filtered off. The crystals were twice washed with distilled water and dried to obtain 19.2 g (96.2%) of compound **IX**, mp 73–74°C [36, 37].

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