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Synthesis of *N*- and *C*-Trimethylsilyl-Substituded Anililes

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Abstract—*N*-Metallation of bromoanilines with ethylmagnesium bromide followed by a reaction with trimethylchlorosilane provided *N*-mono and *N*-bis(trimethylsilyl)bromoanilines depending on the structure of substrate. The metallation of bissilylated bromoanilines with butyllithium permitted the introduction of a trimethylsilyl substituent in the aromatic ring. Previously unknown 2-bromo-*N,N*-bis(trimethylsilyl)aniline, 2,6-dibromo-*N*-trimethylsilylaniline, 2,6-dibromo-N,N-bis(trimethylsilyl)aniline, 2-bromo-6-trimethylsilylaniline, 2-bromo-6-trimethylsilyl-*N,N*-bis(trimethylsilyl)aniline, 2-bromo-6-trimethylsilyl-*N*-trimethylsilylaniline, 2,4,6-tribromo-*N*-trimethylsilylaniline, and 2,4,6-tribromo-*N,N*-bis(trimethylsilyl)aniline were prepared. The structures of the compounds obtained were established by the chromato-mass spectrometry and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.

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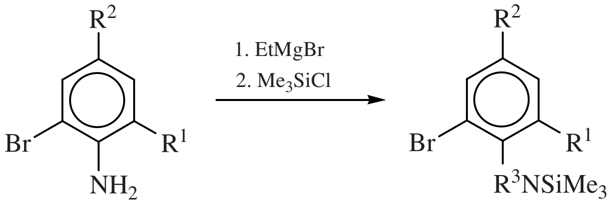
Development of new polymeric materials with desired physicomechanical characteristics is an important problem nowadays. It is solved in particular by preparing new grades of polyolefines. Recently the interest has grown to imine complexes of the transition metals, the components of postmetallocene catalysts of olefins polymerization exhibiting high activity and selectivity. Introduction of substituents containing heteroatoms like silicon in the structure of ligand may increase the thermostability of the catalytic system what is extremely feasible in the olefins polymerization. The catalytic systems with the silicon-containing imine complexes virtually are not documented. *o*-*C*-Silyl-substituted anilines are required for preparation of these complexes. The latter can be obtained from *N*-silyl-substituted anilines. Scanty information exists on both these substances.

N-Trimethyl(triethyl)silyl-substituted anilines are formed by the reaction of aniline with trimethyl- and triethylclorosilanes in 56–80% yield [1, 2]. 2-Bromo (chloro)-*N*,*N*-bis(trimethylsilyl)-substituted anilines are prepared in 43% and 68% yield respectively from the corresponding halogen-containing anilines by treating them with ethylmagnesium bromide, and subsequently, with trimethylchlorosilane [3]. 2-Trimethylsilyl-*N*,*N*-bis(trimethylsilyl)aniline was formed in up to 53% yield in reaction of 2-bromo(chloro)-*N*,*N*-bis (trimethylsilyl)anilines with lithium [3].

The aim of our work was the synthesis of *C*-silyl-substituted anilines. For developing suitable procedure we have studied the silylation of bromoanilines. First we studied the formation of *N*-silyl-substituted anilines by the reaction (1).



(1)

Ia–Ic **IIa–IIf**

I, $R^1 = R^2 = H$ (**a**), $R^1 = Br$, $R^2 = H$ (**b**), $R^1 = R^2 = Br$ (**c**); **II**, $R^1 = R^2 = H$, $R^3 = SiMe_3$ (**a**), $R^1 = Br$, $R^2 = H$, $R^3 = SiMe_3$ (**b**), $R^1 = Br$, $R^2 = R^3 = H$ (**c**), $R^1 = R^2 = Br$, $R^3 = H$ (**d**), $R^1 = R^2 = Br$, $R^3 = SiMe_3$ (**e**), $R^1 = R^2 = H$; $R^3 = SiMe_3$ (**f**).

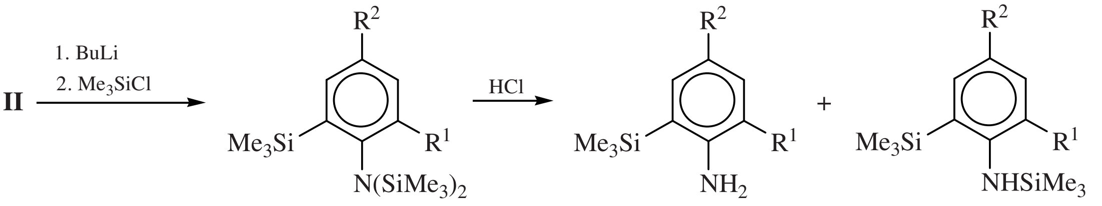
2-Bromo-*N*,*N*-bis(trimethylsilyl)aniline **IIa** was prepared from 2-bromoaniline **Ia** in 40% yield. The attempt to prepare 2,6-dibromo-*N*,*N*-bis (trimethylsilyl)aniline **IIb** from 2,6-dibromoamiline **Ib** failed. We have isolated 2,6-dibromo-*N*-trimethyl-silylaniline **IIc** and only traces of compound **IIb**. The twice prolonged reaction gave insignificant effect, the yield of the compound **IIb** was no more than 6.8%. We have studied the possibility of formation of the compound **IIb** by disproportionation (2) of compound **IIc**. The yield was negligible. For instance, after boiling of 97% compound **IIc.** For 7 h the reaction mixture contained 20% of dibromoaniline **Ib**, 68% of monosilyl-substituted compound **IIc** and only 5% of the disubstituted substance **IIb**.

$$\mathbf{IIc} \rightarrow \mathbf{Ib} + \mathbf{IIb} + \mathbf{IIc}. \qquad (2)$$

Compound **IIb** was isolated in pure state by distillation of the bottoms from several syntheses of compound **IVb**. It formed evidently by *N*-metallation of compound **IIa** with butyllithium followed by the reaction with trimethylchlorosilane and incomplete removal of the silyl protective group.

2,4,6-Tribromoaniline **Ic** gave 2,4,6-tribromo-*N*-trimethylsilylaniline **IId** in 40.9% yield, and the yield of 2,4,6-tribromo-*N*,*N*-bis(trimethylsilyl)aniline **IIe** was not higher than 6.6% similar to the synthesis of compound **IIb**.

C-Silyl-substituted anilines were prepared by reaction (3). The process included metallation of *N*-silyl-substituted anilines **IIa**, **IIb**, **IIe**, and **IIf** with butyllithium, treating the product obtained with trimethylchlorosilane, and removing protective group with methanol or dilute hydrochloric acid.



(3)

IIIa–IIId **IVa–IVd** **Va–Vd**

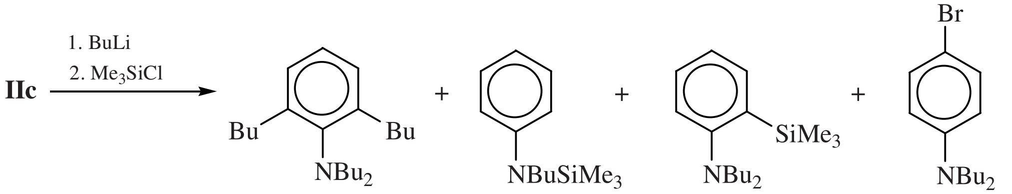
III, $R^1 = R^2 = H$, $R^3 = R^4 = SiMe_3$ (**a**), $R^1 = Br$, $R^2 = H$, $R^3 = R^4 = SiMe_3$ (**b**), $R^1 = Br$, $R^2 = R^3 = R^4 = SiMe_3$ (**c**), $R^1 = R^2 = Br$ (**d**); **IV**, $R^1 = R^2 = H$ (**a**), $R^1 = Br$, $R^2 = H$ (**b**), $R^1 = SiMe_3$, $R^2 = H$ (**c**), $R^1 = SiMe_3$; $R^2 = Br$ (**d**); **V**, $R^1 = Br$, $R^2 = H$ (**a**), $R^1 = Br$, $R^2 = SiMe_3$ (**b**), $R^1 = R^2 = Br$ (**c**), $R^1 = SiMe_3$, $R^2 = Br$ (**d**).

2-Trimethylsilylaniline **IVa** was prepared starting with compound **IIa**. We failed to isolate intermediate 2-trimethylsilyl-*N*,*N*-bis(trimethylsilyl)aniline **IIIa**.

The vacuum distillation of compound **IIb** occurred with decomposition. Therefore we tried to use directly the crude product in the reaction with butyllithium. It turned out that the composition of the reaction products depends on the reagents ratio. At the ratio compound **Ib** : butyllithium 1 : 2.5 and 1 : 4 the main reaction product was 2-bromo-6-trimethylsilylaniline **IVb**, and its yield reached 65%. 2-Bromo-6-trimethylsilyl-*N*,*N*-bis(trimethylsilyl)aniline **IIIb**, 2,6-bis(trimethylsilyl)aniline **IVc**, 2-bromoaniline **Ia**, and 2-bromo-6-trimethylsilyl-*N*-trimethylsilylaniline **Va** were found in the reaction mixture. At larger amount of butyllithium it reacted with trimethylchlorosilane according to equation (4). By the distillation of the reaction mixture in such cases the butyltrimethylsilane was isolated and identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectra.

$$BuLi + Me_3SiCl \rightarrow Me_3SiBu. \qquad (4)$$

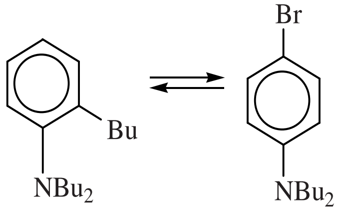
Reaction of compound **IIc** with butyllithium gave 2,5-dibutyl-*N*,*N*-dibutylaniline **VI**, *N*-butyl-*N*-trimethylsilylaniline **VII**, 2-trimethylsilyl-*N*,*N*-dibutylaniline **VIII**, and 4-bromo-*N*,*N*-dibutylaniline **IX**.



(5)

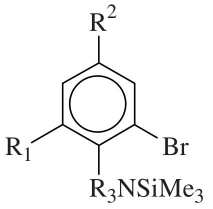
VI **VII** **VIII** **IX**

The formation of compounds **VII–IX** originated from the elimination of one or two bromine atoms. Compound **IX** results from the migration of the second bromine atom from the position 2 to the position 4 with respect to amino group. The rearrangements of this type were described in [4].



(6)

Treating with butyllithium the reaction mixture prepared from compound **Ic** and trimethylchlorosilane resulted in formation of 2,4-dibromo-*N*,*N*-bis(trimethylsilyl)aniline **IIf**, 4-bromo-2,6-bis(trimethylsilyl) aniline **IVd**, 2,4-dibromo-6-trimethylsilyl-*N*-trimethylsilylaniline **Vb**, 2,4-dibromo-6-trimethylsilyl-*N*,*N*-bis (trimethylsilyl)aniline **IIId**, 4-bromo-2,6-bis (trimethylsilyl)-*N*-trimethylsilylaniline **Vc**, 2,4-dibromo-6-trimethylsilyl-*N*-trimethylsilylaniline **Vd**, and of compounds of the general formula **X**, namely, 2,6-dibromo-4-trimethylsilyl-*N*,*N*-bis(trimethylsilyl)aniline **Xa** and 2-bromo-4-trimethylsilyl-*N*-trimethylsilylaniline **Xb**.



Xa–Xb

R^1 = Br, R^2 = R^3 = $SiMe_3$ (**a**); R^1 = R^3 = H; R^2 = $SiMe_3$ (**b**).

Trimethylsilyl group can replace either one or two bromine atoms in *ortho*- and *para*-position, but substitution of three bromine atoms was not observed. The variety of compounds obtained is presumably due to rearrangements occurring in the reaction mixture.

The structures of the compounds obtained were established by chromato-mass spectrometry (Table 1) and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Table 2).

The starting bromo- and dibromoanilines are sufficiently stable to the electron impact, and in their

Table 1. Mass spectra of substituted anilines

Comp. no.	m/z (J_{rel}, %)
Ia	171 (M – 1, 100), 92 (36.5),65(38.5)
Ib	251 (M^+, 100), 170 (5.8), 90 (21.2)
IIa	317 (M^+, 1.1), 302 (9.6), 286(0.1), 271(), 256 (100), 229 (15.4), 214 (23.1), 148 (9.6), 137 (5.8), 73 (7.7)
IIb	395 (M^+, 3.8), 380 (100), 301 (21.2), 286 (13.5), 137 (9.6), 73 (26.9)
IIc	323 (M^+, 34.6), 308 (100), 229 (38.5), 214 (7.7), 148 (19.2), 137 (13.5), 73 (17.3)
IIf	395 (M^+, 2.8), 380 (71.7), 323 (51.9), 308 (100), 292 (14.2), 226 (16.0), 146 (16.9), 73 (64.2)
IIIb	389 (M^+, 1.9), 374 (51.9) 286 (46.2), 220 (100), 73 (44.2)
IIIc	461 (M^+, 1.9), 446 (26.9) 358 (32.7), 292 (100), 204 (11.5), 137 (3.8), 73 (67.3)
IIId	467 (M^+, 3.8), 452 (73.1), 364 (100), 300 (51.9), 139 (13.5), 73 (88.5)
IVc	237 (M^+, 1.9), 222 (9.6), 165 (48.1), 159 (100), 133 (48.1), 74 (13.5)
IVd	317 (M^+, 40.4), 302 (65.4), 286 (7.6), 220 (7.6), 148 (78.8), 137 (7.6), 73 (100)
Va	317 (M^+, 7.6), 302 (100), 286 (0.5), 221 (36.5), 148 (17.3), 137 (9.6), 73 (36.5)
Vb	389 (M^+, 7.6) 374 (100), 317 (7.8), 302 (23.1), 286 (34.6), 220 (44.2), 137 (9.6), 73 (80.8)
Vc	389 (M^+, 16.0), 374 (10.4), 317 (5.7), 300 (5.7), 286 (42.5), 220 (72.6), 73 (100)
Vd	395 (M^+, 26.9), 380 (36.5), 226 (9.6), 146 (13.5), 73 (100)
VI	315 (M^+ – 2, 0.1), 215 (96.2), 159 (100), 103 (11.5), 61 (13.5)
VII	277 (M^+, 1.9), 231 (46.2), 175 (100), 119 (98.1), 105 (17.3), 73 (17.3)
VIII	219 (M^+ – 2, 1.9), 187 (88.5), 131 (100), 103 (19.2), 75 (21.5)
IXa	395 (M^+, 7.5), 380 (100), 301 (31.1), 286 (14.1),220 (4.7),139 (12.3), 73 (49.1)
IXb	317 (M^+, 66.0), 302 (66.1), 286 (3.6), 221 (100), 206 (73), 148 (42.3), 137 (9.6), 73 (38.5)

mass spectra molecular ion peak has the greatest intensity. Main fragment ions are formed by elimination of bromine. Intensities of peaks of the molecular ions in the mass spectra of compounds obtained vary in a broad range, 0.1–66%.

Mass spectra of *C*-silyl-substituted anilines contain up to 100% of ion with *m*/*z* 73 corresponding to trimethylsilyl group. Such decay is not characteristic of *N*-substituted anilines. More often elimination of the methyl group occurs. The bromine atom having *o*-location with respect to trimethylsilyl group forms a species $[Me_2SiBr]^+$ with *m*/*z* 137–139 units. Among the other pathways of fragmentation note the elimination of 96 (Br + Me), 169 (Me_3Si + Br + Me), 109 (Br + 2Me), 103 (Me_3Si + 2Me), and 155 (Me_3Si + Br) mass units.

Attribution of signals in the ^1H, ^{13}C, and ^{29}Si NMR spectra presented in Table 2 and in Eperimental is based on the analysis of spectra of pure compounds and their mixtures considering the multiplicity and the integral intensity of proton signals in ^1H NMR spectra, and the chemical shifts of signals and their relative intensity in ^{13}C(APT) and ^{29}Si NMR spectra. The two-dimentional COSY, HSQC, and HMBC procedures were used including 2D-correlations ^1H–^{29}Si for the attribution of signals of $SiMe_3$ groups. Note that at the successive substitution of protons in the NH_2 group of 2,6-dibromoaniline **Ib** with trimethylsilyl groups (products **IIb** and **IIc**) the chemical shift of the quarternary carbon atom C_2–Br was the most strongly affected (108.82, 116.36, and 127.82 ppm).

EXPERIMENTAL

2-Bromoaniline, 2,6-dibromoaniline, and 2,4,6-tribromoaniline were prepared according to [5].

Table 2. ^1H, ^{13}C, and ^{29}Si(XC) chemical shifts ($CDCl_3$, 27°C).

Comp. no.	^1H, δ, ppm, number of atoms						
	The number of atom in aniline				NH, NH_2	N–$SiMe_3$	C–$SiMe_3$
	3	4	5	6			
Ia	7.40 d 1H	6.62 t 1H	7.10 t 1H	6.75 d 1H	4.1 br 2H		
Ib	7.36 d 1H	6.48 t 1H	7.36 d 1H		4.56 2H		
IIa	7.57 d 1H	6.93 t 1H	7.17 t 1H	7.02 d 1H		0.128 s 18H	
IIb	7.54 d 1H	6.75 t 1H	7.54 d 1H			0.2 s 18H	
IIc	7.43 d 1H	6.56 t 1H	7.43 d 1H		3.6 1H	0.35 s 9H	
IId	7.56 s 1H		7.56 s 1H		3.75 1H	0.30 s 9H	
IIe	7.66 s 1H		7.66 s 1H			0.17 s 18H	
IIIb	7.58 d 1H	6.91 t 1H	7.43 d 1H			0.19 s 18H	0.35 s 9H
IVa[a]	7.19 t 1H	6.79 t 1H	7.32 d 1H		3.72 br 2H		0.36 9H
IVb	7.45 d 1H	6.63 t 1H	7.24 d 1H		4.3 2H		0.37 s 9H
Va	7.50 d 1H	6.73 t 1H	7.27 d 1H		3.5 1H	0.34 s 9H	0.35 s 9H
IX[c]	6.52 m 2H			6.48 m 2H			

Table 2. (Contd.)

Comp. no.	^{13}C, δ, ppm								^{13}Si, δ, ppm	
	The number of atom in aniline						N–SiMe$_3$	C–SiMe$_3$	N–SiMe$_3$	C–SiMe$_3$
	1(C–N) quart.	2(C–Br) quart.	3	4	5	6				
Ia	144.04	109.28	132.55	119.35	128.28	115.70				
Ib	141.96	108.82	131.71	119.34	131.70	108.82				
IIa	147.16	126.84	132.98	125.14	127.56	131.81	1.88		6.17	
IIb	147.30	127.82	132.21	125.62	132.21	127.82	2.56		7.78	
IIc	144.29	116.36	132.25	121.58	132.25	116.36	1.82		8.58	
IId										
IIe										
IIIb	151.22	127.89	134.69	124.81	134.86	143.29 C–Si	3.22	2.25	5.85	–3.10
IVa^{a}	151.31	115.28^{b}		118.31		122.62 C–Si		–0.79		–5.59
IVb	147.92	110.56	134.08	119.15	133.79	124.40 C–Si		–0.89		–4.41
Va										
IX^{c}	158.73 quart.			142.53 quart.						

[a] For the convenience of comparison the numbering of carbon atoms in compound **IVa** differs from the standard one: C_6 is the quarternary carbon atom adjacent to SiMe$_3$. Chemical shift of the proton H^2 6.64 ppm (doublet, 1H); the signals of CH-carbon atoms C_3 and C_5 (134.98 and 130.48) are not attributed. [b] CH-carbon atom. [c] The multiplets $H_{2,6}$ and $H_{3,5}$ of the AA'BB' spin system of protons in aniline (6.52 and 6.48 ppm) are not attributed. The signals of CH-carbon atoms in aniline $C_{2,6}$ and $C_{3,5}$ (130.40 and 120.46 ppm) are not attributed. The signals of the quarternary carbon atoms in aniline C_1 and C_4 (142.53 and 158.73 ppm) are not attributed. The signals of protons of *n*-Bu group, δ, ppm: 0.94 (6H, Me), 1.39 (4H, CH$_2$), 1.55 (4H, CH$_2$), 2.55 (4H, NCH$_2$). The signals of carbon atoms of *n*-Bu group, δ_C, ppm: 13.89 (Me), 22.92 (CH$_2$), 32.21 (CH$_2$), 34.16 (NCH$_2$).

GLC analysis was carried out on a Tsvet-500 chromatograph, 2000 × 3 mm column, stationary phase 15% of PMS-2000 on Chromaton *N*-AW-DMCS, particle size 0.250–0.315 mm, temperature of the vaporizer and the detector 280°C, the detector current 100 mA, ramp from 50°C to 280°C at a rate 12 deg min^{-1}, carrier gas helium, flow rate 50 ml min^{-1}.

Mass spectra were obtained on a Hewlett–Packard HP-5971A mass spectrometer at the ionizing voltage 70 V. For the separation of compounds a quartz 25000x0.32 mm capillary column was used, the stationary phase the DB-5 methylphenylsiloxane elastomer, thickness of the film 25 nm. Analyses were carried out at ramp from 50 to 280°C at a rate 7 deg min^{-1}, carrier gas helium.

^{1}H, ^{13}C, and ^{29}Si NMR spectra were taken from solutions in CDCl$_3$ on a Bruker AVANCE-600 spectrometer, operating frequencies 600 MHz (^{1}H), 150.9 MHz (carbon atoms), 119.2 MHz (silicon atoms) respectively.

2-Bromo-*N*,*N*'-bis(trimethylsilyl)aniline (IIa). A solution of 10.3 g of 2-bromoaniline in 60 ml of ether was treated with a solution of ethylmagnesium bromide prepared from 3.5 g of magnesium and 11.2 ml of ethyl bromide in 50 ml of ether. The mixture obtained was refluxed for 4 h, and 18.3 ml of trimethylchlorosilane was added to the reaction mixture in the course of 0.5 h. After that the resulting mixture was refluxed for 8 h and the precipitate was filtered off under nitrogen. Ether was distilled from the filtrate, and the residue was distilled in a vacuum to give 7.6 g (40%) of the compound **IIa**, bp 130–135°C, n_D^{20} 1.5185.

2,6-Dibromo-*N*-trimethylsilylaniline (IIc). This compound was prepared analogously from 15.3 g of

2,6-dibromoaniline and the above-mentioned amounts of other reagents to give 10.5 g (53.3%) of compound **IIc** with the main substance content 97.6%, bp 101–102°C (2 mm Hg), n_D^{20} 1.5720, and 0.9 g of the fraction with bp 120–130°C (2 mm Hg), n_D^{20} 1.591 characterized as a mixture of 5% of compound **Ib**, of 43% of compound **IIc** and 47% of compound **IIb**.

Disproportionation of compound (IIc). Compound **IIc** with the main substance content 97% was heated at 50–60°C. After 12 h of heating the reaction mixture contained 12.2% of dibromoaniline, 78.8% of the starting compound, and 3.2% of compound **IIb**. After additional 7 h the reaction mixture contained 20% of dibromoaniline, 68% of the starting compound, and 5% of compound **IIb**.

2,4,6-Tribromo-*N*-trimethylsilylaniline (IId) was prepared analogously to **IIa** from 0.045 mol of compound **Ic** and the above-mentioned amounts of other reagents. Distillation of the reaction mixture gave 8.8 g of a substance of bp 110–120°C (2.5 mm Hg), n_D^{20} 1.5755, consisting to 84% of the product **IId** (yield 40.9%) and to 16% of the compound **IIe**.

2-Trimethylsilylaniline (IVa). To a solution of 8.1 g of compound **IIa** in 50 ml of ether 0.046 mol of butyllithium was added at –59 to –60°C under the nitrogen flow, and the reaction mixture was kept for 1 h at –40°C to –60°C. At –20°C 3.3 ml of trimethylchlorosilane was added to the mixture obtained, and the resulting mixture was left overnight. After that it was treated at –5°C to –7°C with 40 ml of 5% hydrochloric acid, ether layer was separated, and water layer was extracted with ether (2 × 15 ml). Ether was distilled off, and the residue was distilled in a vacuum to give 2.0 g (46.6%) of product **IVa** with bp 104–110°C (4–5 mm Hg), n_D^{20} 1.524.

2-Bromo-5-trimethylsilylaniline (IVb). A solution of the product **IIb** prepared from 0.029 mol of dibromoaniline, ethylmagnesium bromide, and trimethylchlorosilane in 30 ml of ether according to the above-described procedure, was treated with a solution of 0.075 mol of butyllithium in 70 ml of ether (dibromoaniline:butyllithium molar ratio 1:2.5) at –40 to –60°C for 1 h 40 min and kept for 1 h at this temperature. Thereafter 4 ml of trimethylchlorosilane were added in the course of 5 min at –30°C. The mixture obtained was left overnight, and then 30 ml of 7% hydrochloric acid was added to it at –5°C to –10°C. Ether layer was separated and the water layer was extracted with ether. Combined ether solution were dried over zeolites, ether was removed, and the residue was distilled in a vacuum to give 4.8 g (67.9%) of compound **IVb**, bp 145–150°C (4 mm Hg), n_D^{20} 1.5615.

The reaction mixture contained also the products **IIIb** and **Va**.

The vacuum distillation of a mixture obtained by trimethylsilylation of 0.029 mol of dibromoaniline in 30 ml of ether and treated with a butyllithium solution under the above-described conditions but at 1:4 dibromoaniline/butyllithium molar ratio provided 4.6 g (65%) of compound **IVb** with the main substance content 98%, bp 135–140°C (5 mm Hg), n_D^{20} 1.5615. Besides, 4.7 g of the volatile products were collected in the trap. Repeated distillation of the latter gave 3.8 g of butyltrimethylsilane, bp 93–94°C, n_D^{20} 1.4030.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm: -0.05 s (9H, $SiMe_3$), 0.47 m (2H, CH_2Si), 1.30 m (2H, CH_2), 1.25 m (2H, CH_2), 0.86 t (3H, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –1.72 ($SiMe_3$), 16.39 (CH_2Si), 26.55 (CH_2), 26.17 (CH_2), 13.77 (CH_3). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: 1.6.

The reaction mixture contained also compounds **IIIb, IVb,** and **Va**. The distillation of bottoms from several syntheses gave 4.7 g of compound **IIb**, bp 165–170°C (4 mm Hg), n_D^{20} 1.542

In a reaction mixture prepared analogously from 0.01 mol of tribromoaniline and 0.8 mol of butyllithium and worked up as described above compounds **IIf, IVd, Vb, IIId, Vc,** and **Vd** and also substances **Xa** and **Xb** were found.

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REFERENCES

1. Kashutina, M.V., Ioffe, S.L., and Tartakovskii, V.A., *Usp. Khim.*, 1975, vol. 44, no. 9, p. 1620.
2. Anderson, H.H., *J. Am. Chem. Soc.*, 1951, vol. 73, no. 12, p. 5802.
3. Eaborn, C. and Pande, K.C., *J. Chem. Soc.*, 1961, p. 297.
4. *Obshchaya organicheskay khimiya* (Comprehensive Organic Chemistry), Kochetkov, N.K., Ed., Moscow: Khimiya, 1982, vol. 1, p.706.
5. *Sintezy organicheskikh preparatov* (Organic Syntheses), Kazanskii, B.A., Ed., Moscow: Inostrannaya Literatura, 1952, issue 3, p. 236.