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SOME CHARACTERISTICS OF SILYLATING AMINOPHENOLS

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Silylated compounds are finding wider and wider use in organic chemistry, in particular in the synthesis of high-molecular-weight compounds [1]. The use of silylated functional compounds [2] permits one to vary broadly the conditions for the synthesis and the properties of polymers with a heterocyclic structure, for example polybenzoxazoles [3].

In view of the insufficient data on the silylation of bis-o-aminophenols and the polycondensation in which their silylated derivatives have participated, it became of interest to study these processes in more detail on model compounds. In connection with this the silylation of o-, m-, and p-aminophenols with trimethylsilyldiethylamine and the conversion of their silylation products were investigated in this paper.

The investigation of the composition and structure of the products from the silylation of o-, m-, and p-aminophenols with trimethylsilyldiethylamine by IR, PMR, ^{13}C NMR spectroscopy, and GLC showed that it leads to a mixture of O-trimethylsilyl- and N,O-bis(trimethylsilyl)aminophenols (Table 1).

$$HOC_6H_4NH_2 + Me_3SiNEt_2 \rightarrow Me_3SiOC_6H_4NH_2 + HNEt_2 \qquad (1)$$

$$HOC_6H_4NH_2 + 2Me_3SiNEt_2 \rightarrow Me_3SiOC_6H_4NHSiMe_3 + 2HNEt_2 \qquad (2)$$

The O-trimethylsilylaminophenols evolved by the reaction with trimethylsilyldiethylamine are converted into N,O-bis(trimethylsilyl)diethylaminophenols [4]

$$Me_3SiOC_6H_4NH_2 + Me_3SiNEt_2 \rightarrow Me_3SiOC_6H_4NHSiMe_3 + HNEt_2 \qquad (3)$$

After the subsequent reaction of O-trimethylsilylaminophenols with 2 moles of ethylmagnesium bromide and trimethylchlorosilane [5], O-trimethylsilyl-, N,O-bis(trimethylsilyl)-, and N,N,O-tris(trimethylsilyl)aminophenols were detected in the reaction mixture

$$Me_3SiOC_6H_4NH_2 - \left| \begin{array}{l} \xrightarrow[-2C_2H_6]{2EtMgBr} Me_3SiOC_6H_4N(MgBr)_2 \xrightarrow[-2MgBrCl]{2Me_3SiCl} Me_3SiOC_6H_4N(SiMe_3)_2 \\ \\ \xrightarrow[-C_2H_6]{EtMgBr} Me_3SiOC_6H_4NH(MgBr) \xrightarrow[-MgBrCl]{Me_3SiCl} Me_3SiOC_6H_4NHSiMe_3 \end{array} \right. \qquad (4)$$

The N,O-bis(trimethylsilyl)aminophenols, according to the GLC data of the original and final products, transilylate the aminophenols

$$Me_3SiOC_6H_4NHSiMe_3 + HOC_6H_4NH_2 \rightarrow 2Me_3SiOC_6H_4NH_2 \qquad (5)$$

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TABLE 1. Silylation of Aminophenols with Trimethylsilyldiethylamine

Aminophenol	Mole ratio Me_3SiNEt_2 : aminophenol	Relative yield of silylation products, % (GLC)	
		O-trimethylsilylaminophenol	N,O-bis(trimethylsilyl)aminophenol
o-$HOC_6H_4NH_2$	0,5	99	1
	1	82	18
	2	42	58
	3	8	92
m-$HOC_6H_4NH_2$	1	95	5
	2	21	79
p-$HOC_6H_4NH_2$	1	100	–
	2	23	77

TABLE 2. Composition of Mixtures of O-Trimethylsilyl-, N,O-Bis-(trimethylsilyl)-, and N,N,O-Tris(trimethylsilyl)aminophenols as a Function of the Conditions for the GLC Separation of the Reaction Products of (4)

Isomers of aminophenol	GLC conditions				Relative composition of mixture, %			
	sample size, μmole	column		T., °C	gas, ml/min	O-trimethylsilylaminophenol	N,O-bis(trimethylsilyl) aminophenol	N,N,O-tris(trimethylsilyl) aminophenol
		length, m	diameter, mm					
ortho	2	1	2,5	150	66,6	10	54	36
	500	2,6	9	200	200	1	72	27
meta	2	1	2,5	150	66,6	20	40	40
	300	2,6	9	200	200	1	76	23
para-	2	1	2,5	150	66,6	8	5	87
	200	2,6	9	200	200	1	18	81

The N,N,O-tris(trimethylsilyl)aminophenols can also react with the O-trimethylsilylaminophenols; this is observed during the GLC separation of the reaction (4) products under various conditions (Table 2)

$$Me_3SiOC_6H_4N(SiMe_3)_2 + Me_3SiOC_6H_4NH_2 \rightarrow 2MeSiOC_6H_4NHSiMe_3 \qquad (6)$$

It was established by the silylation of o-aminophenol with an insufficiency of trimethylsilyldiethylamine (1: 0.5 mole) that the content of the initially formed N,O-bis(trimethylsilyl)-o-aminophenol steadily decreases after all of the silylating reagent is consumed (Fig. 1). Consequently, reactions (1), (3), and (5), and possibly (2) proceed in parallel in every case during the silylation of aminophenols with trimethylsilyldiethylamine.

The properties of the silylated aminophenols isolated by preparative GLC are given in Tables 3 and 4.

N,O-Bis-(trimethylsilyl)-o-aminophenol simulates the synthesis of polysiloxyamides [3] by reacting with benzoyl chloride and is converted to the o-siloxyanilide derivative of benzoic acid

$$o\text{-}Me_3SiOC_6H_4NHSiMe_3 + PhCOCl \rightarrow o\text{-}Me_3SiOC_6H_4NHCOPh + Me_3SiCl \qquad (7)$$

As a result of a similar reaction between O-trimethylsilyl-o-aminophenol and benzoyl chloride, the o-siloxyanilide derivative of benzoic acid which is initially formed splits off the Me_3Si groups with the HCl given off and the o-hydroxyanilide derivative of benzoic acid is obtained

$$o\text{-}Me_3SiOC_6H_4NH_2 + PhCOCl \rightarrow o\text{-}Me_3SiOC_6H_4NHCOPh + HCl \rightarrow o\text{-}HOC_6H_4NHCOPh + Me_3SiCl \qquad (8)$$

The structure of the o-siloxy- and o-hydroxyanilide derivatives of benzoic acid was confirmed by the PMR and IR spectral and elemental analysis. The trimethylchlorosilane given off was identified by GLC.

TABLE 3. Properties of the Silylated Aminophenols

Compound	Position of substituents	bp, °C	n_D^{20}	d_4^{20}	IR spectrum, ν, cm^{-1}			
					NH_2 (NH)	ArOSi	ArNSi	SiNSi
$Me_3SiOC_6H_4NH_2$	ortho	229	1,5142	0,9911	3385 3480	925	–	–
	meta	249	1,5226	1,0010	3385 3460	980	–	–
	para	250	1,5190	1,0011	3370 3345	215	–	–
$Me_3SiOC_6H_4NHSiMe_3$	ortho	247	1,4897	0,9310	3405	930	905	–
	meta	268	1,5003	0,9481	3390	1005	905	–
	para	270	1,4974	0,9448	3400	925	910	–
$Me_3SiOC_6H_4N(SiMe_3)_2$	ortho	274	1,4807	0,9203	–	940	910	975
	meta	280	1,4767	0,9092	–	990	905	975
	para	283	1,4743	0,9086	–	935	910	975

TABLE 4. Parameters of the PMR Spectra of the Silylated Aminophenols (in CCl_4)

Compound	Position of substituents	δ, ppm and assignment			
		C_6H_4	NH_2(NH)	$OSiMe_3$ *	$N(SiMe_3)_2$
$Me_3SiOC_6H_4NH_2$	ortho	6,68	3,48	0,21	–
	meta	6,26	3,58	0,17	–
	para	6,72	3,34	0,17	–
$Me_3SiOC_6H_4NHSiMe_3$	ortho	6,70	3,82	0,22	–
	meta	6,26	3,32	0,18	–
	para	6,72	3,16	0,16	–
$Me_3SiOC_6H_4N(SiMe_3)_2$	ortho	6,80	–	0,28	0,03
	meta	6,28	–	0,18	0,03
	para	6,73	–	0,18	0,03

*The chemical shifts of the protons in the $OSiMe_3$ and $NSiMe_3$ groups for the N,O-bis(trimethylsilyl)aminophenols coincide.

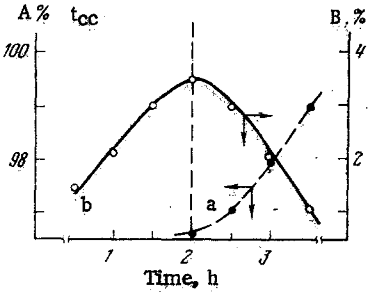

Fig. 1. Dependence of the O-trimethylsilyl-o-aminophenol (a) and N,O-bis(trimethylsilyl)-o-aminophenol (b) content in the products of the silylation of o-aminophenol with trimethylsilyldiethylamine (1 : 0.5 mole) on time. A) O-Trimethylsilyl-o-aminophenol content; B) N,O-bis(trimethylsilyl)-o-aminophenol; t_{cc} is the time spent for the complete consumption of the silylating agent.

EXPERIMENTAL

The PMR spectra were run on a Perkin–Elmer spectrometer (60 MHz, internal standard HMDS); the IR spectra on a UR-20 instrument. The GLC analysis was carried out on a Tsvet 4-67 chromatograph in a He stream (66.6 ml/min), column 1 m × 2.5 mm packed with 20% E-301 on Chromosorb W (50-60 mesh) at 150°C with a katharometer detector. The preparative separation of the silylated aminophenols was carried out using an attachment developed at the Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, column 2.6 m × 9 mm packed with 20% E-301 on Chromosorb W (50-60 mesh); He, 200 ml/min, 180-220°C.

Silylation of Aminophenols (general method). The aminophenol, 57.2 g (0.525 mole), and 200 ml (1.05 mole) of trimethylsilyldiethylamine were mixed for 3.5 h at 120°C in an Ar atmosphere while distilling off the diethylamine formed, and then the product obtained was vacuum distilled in an Ar stream.

Benzoylation of the Silylated o-Aminophenols. A solution of 3.17 g (0.0125 mole) of N,O-bis(trimethylsilyl)-o-aminophenol in 125 ml of freshly distilled CH_2Cl_2 was cooled with a mixture of dry ice and acetone and a solution of 1.76 g (0.0125 mole) of benzoyl chloride in 125 ml of CH_2Cl_2 cooled with the same mixture was added. The temperature of the reaction mixture was raised to ~20°C within 1 h and then the solvent was removed in vacuo.

o-Siloxyanilide Derivative of Benzoic Acid. PMR spectrum (δ, ppm): 0.22 ($OSiMe_3$), 6.67 (C_6H_4), 7.73 (C_6H_5). IR spectrum (ν, cm^{-1}): 1660 (amide I), 1530 (amide II), 3400 (NH), 925 (PhOSi), 1250 ($SiCH_3$). Found: C 66.91; H 6.73; Si 10.09%. $C_{16}H_{19}NSiO_2$. Calculated: C 67.33; H 6.71; Si 9.84%.

o-Hydroxyanilide Derivative of Benzoic Acid. PMR spectrum (δ, ppm): 1550 (amide II), 3410 (NH), 2600-3300 (OH). Found: C 73.22; H 5.30%. $C_{13}H_{11}NO_2$. Calculated: C 73.22; H 5.20%.

CONCLUSIONS

1. The silylation of o-, m-, and p-aminophenols with trimethylsilyldiethylamine and the conversion of their silylation products were studied.

2. The following were isolated and characterized: o-, m-, and p-$Me_3SiOC_6H_4NH_2$; o-, m-, and p-$Me_3SiOC_6H_4NHSiMe_3$; and o-, m-, and p-$Me_3SiOC_6H_4N(SiMe_3)_2$.

3. The o-hydroxyanilide and o-siloxyanilide derivatives of benzoic acid respectively were obtained by reacting O-trimethylsilyl-o-aminophenol and N,O-bis(trimethylsilyl)-o-aminophenol with benzoyl chloride.

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