ORGANOBORON COMPOUNDS

359. REACTION OF 2-PYRIDYLAMINOBORANES WITH ISOCYANATES AND ISOTHIOCYANATES

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In the series of aminoboranes the 2-pyridylaminodialkylboranes differ by their ability to form cyclic coordination compounds by adding to ethoxyacetylene at the $C \equiv C$ bond [1, 2], and to aldehydes, ketones, and CO_2 at the C=O bond [1, 3]. 2-Pyridylaminodiphenylborane behaves analogously with respect to carbonyl compounds [4, 5].

An investigation of the reactions of 2-pyridylaminoboranes with isocyanate and isothiocyanates is reported in this paper. It is known that urea and thiourea derivatives are formed when amines react with isocyanates and isothiocyanates. 2-Pyridylureas and 2-pyridylthioureas are synthesized this way from 2-aminopyridine [6]. At the same time, many compounds with N-E bond (E = Si, Ge, Sn, Al, Zn, etc.) also add to isocyanates and isothiocyanates at the C=N bond [7]:

$$X_{n}E - NR_{2} + R' - N = C = Y \rightarrow X_{n}E - N - C - NR_{2}$$

$$\| Y$$

$$n = 1, 2, 3; Y = 0, S.$$

Reactions of a similar type have also been described for the series of aminoboranes [7-10]. Therefore, we naturally expected that the reaction of the 2-pyridylaminoboranes (I) with isocyanates would lead to N-dialkyl-boryl-N'-(2-pyridyl)ureas possessing a chelate structure (II). It turned out that (I) react with isocyanates in petroleum ether or benzene at ~20°C forming yellow crystalline substances in good yields. The compounds obtained have a chelate structure, which is confirmed by the ¹¹C NMR spectra (signals in the tetracoordinated B region) and the mass spectra (the absence of molecular ions and the presence of characteristic ions with m/e (M - R)⁺ [11]). However, as further investigations showed, the products of the reaction between (I) and the isocyanates have structure (III), which differs from (II) by the presence of the pyridonimine fragment instead of the aminopyridinone. The formation of chelates (III) evidently proceeds through a six-center cyclic transition state, and as a result, a rearrangement of the aminopyridine system to a pyridonimine system takes place



Compounds (III) differ in their chemical and physical properties from (II), which we previously obtained based on the reactions of organoboranes with (2-pyridyl)ureas [12]. The 1-carbamoylpyridon-2-imine hydro-chlorides (IV) and not the (2-pyridyl)ureas, whose formation was to be expected in the case of chelates (II), were isolated after reacting an alcoholic HCl solution with (III):

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										R I	Ŕ	R ¹ /H ²	(II	
Com-					Solvent	Yield,	mp, °C	¹¹ B NMR spectrum.	Empirica1	Fou	nd/Cal	culated	%	
pound	×	μ ²	Å	K		9/o	(solvent) ⁴	<pre> ô, ppm (sol- vent, t^cC) </pre>	formula	c	H	В	z	ថ
							148-149	2.0		65.54	9.68	3.95	15.26	
(IIIa)	C ₄ H ₉	Π	Н	CH3	Hexane	82 6	(hexane)	(THF, 60)(C45H26BN30 B	65,52	9,53	3,94	15,28	ţ
/1114/	Þ.	11	n	пJ	ā	ų	(130-132)	2,0	ОМАЛУ	71,03	8,35	3,04	12,72	
(arri)	61170	5	4	CIENS	*	P n	(allazian)	(THF, 20)	C201128DIN3U	71,22	8,37	3,21	12,46	1
(111)	Ц	11	ξ	- HJ	4	60.6	124-125	2.5	C. H. BCIN OF	58,03	8,30	3,52	13,31	11,50
(arri)	61177	1	3	ŝm	*	2	(ethanol)	(THF, 20)	~1511251JU113U	58, 19	8,14	3,40	13,57	11,45
(PIII)	Д	1	5	-H-C	Donron o	69	125-126	1,5	C U BCIN O	64,37	7,21	2,96	11,37	9,64
(nTTT)	6111/22	=	5	C61155	perizence	5	(ethanol)	(UN, '00)	0201121100120	64,62	7,32	2,91	11,30	9,54
(111.0)	пJ	ר ה כה	11	CH	Horono	70	132 - 134	-0,8	C H BN O	71,05	8,39	3,14	12,00	1
(ATTI)	C3117	C6115U112	q	1	nexalle	T.C	(nexane)	(.1.HF, 60)	U2011281113U	71,22	8,36	3,21	12,46	l
/ 1116 /	р С	п		τυυ"	3	я	136-140	1,0		71,66	8,56	3,01	12,39	
(1111)	dulla.	=	=	0-011306114	*	3	(penzene)	(THF, 60)	V21II30101/3U	71,80	8,61	3,08	11,96	ſ
(~111/	П	п	H	" UU UU H	Bonzono	64	135-137	2,2	C NG A J	66,98	7,69	3,33	12,76	-
(SIII)	C3117	1	#	h-ullious		1	(etnanol)	(THF, 80)	C1911261113U2	67,27	7,72	3,19	12,39	ł
(1111)	ţ	-			a	14	126-127	1.8	O N DOI 11 D	56,89	5,83	2,93	11,15	18,90
	C3.D7	5	H	10-01, p-01-00113		5	(Leulano)	(THF, 70)	U18H122DU12IV3U	57,18	5,87	2,86	11,11	18,75
/1112	Ľ	1	t			о И	278-280	1.7	O NG II O	76,41	5,38	2,95	11,08	
(1111)	Cents	4	H	1 C6II5	CID2CI2	3	(benzene)	(THF, 20)	C24H20DIN3C	76,41	5,34	2,87	11,14	Į.
aThe w	 Laiori	tv of co	mnor	inds melts wit	փ ժերուու	osition								

TABLE 1. Chelate Boron Compounds with 1-Carbamoylpyridon-2-imines as the Ligands

^aThe majority of compounds melts with decomposition. ^bThe substance was obtained from crude 2-pyridylaminodialkylborane and the yield is based on the original 2-

aminopyridine. ^OPMR spectrum in CDCl₃ (5, ppm): 8.35 m (H⁶), 7.15 m (H⁴), 6.55 m (H³), 5.92-6.28 m (H⁵ + NH), 2.78 s (CH₃N). ^OPMR spectrum in CDCl₃: 8.42 d (H⁶), 7.18 m (H⁴), 6.54 d (H³), 6.08 Br. s (NH), 2.95 s (CH₃).



The PMR, IR, and UV spectra also support structure (III). Thus, the signal in the PMR spectra for H⁶ in the pyridine fragment is located at a weaker field (~8.25 to 8.50 ppm) compared to H³, H⁴, and H⁵ (~6.00 to 7.40 ppm), whereas the signals of the H⁶ and H⁴ protons for the 1-methylpyridon-2-imine-tripropylborane complex are close (multiplet with a center at 7.22 ppm [13]). This is evidently connected with the deshielding action of the C=O group in relation to which the H⁶ proton in (III) is located in the periposition (see the review in [14]). No such effect is observed for compounds of type (II). The band at 1660 cm⁻¹ (ν C=N) in the IR spectra of chelates (III) is characteristic along with the intense absorption band of the C=O group at 1715 cm⁻¹. An absorption in this region was observed in the spectrum of the above-mentioned 1-methylpyridon-2-imine complex with tripropylborane and was also ascribed to the vibrations of the imino group [13].

Since the 1-carbamoylpyridon-2-imines are thus the chelate-forming ligands in (III), they are suitably called 1-carbamoylpyridon-2-iminates. The synthesized (III) (Table 1) are stable in air, soluble in THF, ether, $CHCl_3$, and easily crystallized in abs. EtOH.

The addition of (I) to isocyanates is an interesting example of the synthesis and stabilization of a nonstandard ligand as a result of chelate formation. It should be mentioned that the 1-carbamoylpyridon-2-imines (and also their derivatives) were not previously known and evidently cannot be prepared directly from 2-aminopyridine and isocyanates. However, the 1-carbamoylpyridon-2-imine hydrochlorides (IV), as was shown above, can be synthesized from 2-aminopyridine using trialkylboranes through (I) and (III). We previously used the formation of chelate boron compounds at an intermediate step to obtain N-acylamidines from amides and nitriles [15], and also 9-alkyl-1,2,3,4-tetrahydroacridines from the anil of cyclohexanone and nitriles [16].

Salts (IV) are solid colorless substances which are very unstable and hard to store. When heated, they easily decompose into the isocyanates and 2-aminopyridine hydrochloride. The effect of boiling CH_3OH on (IV) yields methyl N-methylcarbamate and the corresponding 2-aminopyridine hydrochlorides

$$CH_{3}NHC-N \bigvee_{\substack{0\\ 0\\ NCH_{2}C_{2}H_{4}} \cdot HCl} \xrightarrow{CH_{3}OH} CH_{3}NHCOCH_{3} + \bigvee_{N} -NHCH_{2}C_{6}H_{5} \cdot HCl$$

The salts of the (2-pyridyl)ureas isomeric to (IV) on the other hand possess much greater thermal and chemical stability.

The pyridylaminoboranes (I) add to isothiocyanates forming chelate compounds evidently having a structure analogous to (III). Thus, dibutylboryl-[1-(allylthiocarbamoyl)pyridon-2-iminate] (V) was obtained from 2-pyridylaminodibutylborane and allylisothiocyanate with an 89% yield



Chelate (V) is a yellow crystalline substance highly soluble in the majority of organic solvents. The signal of the terminal H^6 proton in the PMR spectrum of (V) is shifted toward the weak field (δ 9.52 ppm) even more than in that of (III) because of the deshielding effect of the thiocarbonyl group.

EXPERIMENTAL

The operations were carried out in a dry N_2 atmosphere. The PMR spectra were run on a Varian DA 60-IL instrument (TMS was the internal standard), and the ¹¹B NMR spectra on a PC 56/19 instrument. The IR spectra were run on a UR-20 spectrometer. The original 2-pyridylaminodialkylboranes and 2-pyridyl-aminodiphenylborane were obtained by the methods in [2].

<u>Dialkylboryl-(1-carbamoylpyridon-2-iminates) (IIIa-h).</u> To a solution of 0.01-0.05 mole of the 2-pyridylaminodialkylborane in hexane or benzene (the crude product of the reaction between the trialkylborane and 2-aminopyridine can be used) was added an equimolar amount of the isocyanate. The precipitated crystals of (III) were filtered off, washed, and recrystallized from the appropriate solvent (see Table 1).

<u>Diphenylboryl-[1-(phenylcarbamoyl)pyridon-2-iminate] (IIIi)</u>. To a suspension of 1.7 g of 2-pyridylaminodiphenylborane in 40 ml of CH_2Cl_2 was added 1 ml of phenylisocyanate and it was mixed at 40°C until the solid dissolved completely. The solvent was distilled off, the residue washed with EtOH, and IIIi was isolated. IR spectrum in CH_2Cl_2 (ν , cm⁻¹): 1654 (C=N), 1712 (C=O), and 3396 (NH).

<u>1-(Methylcarbamoyl)pyridon-2-imine Hydrochloride (IV, $R^2=R^3=H$, $R^4=CH_3$).</u> To a solution of 8.3 g of chelate (IIIa) in 120 ml of abs. ether was added with agitation a solution of 0.045 mole of HCl in BuOH. It was boiled until the mixture was completely decolorized. The precipitate was filtered off and washed with ether. 1-(Methylcarbamoyl)pyridon-2-imine hydrochloride, 5.5 g (98%), was obtained, mp 83-85°C. Found: C 44.73; H 5.56; Cl 19.02; N 21.33%. C₇H₁₀ClN₃O. Calculated: C 44.81; H 5.37; Cl 18.89; N 22.40%. PMR spectrum in CD₃OD (δ , ppm): 7.73-8.07 m and 6.72-27 m (ring CH), 2.96 s (N-CH₃).

<u>Thermal Decomposition of 1-(Methylcarbamoyl)pyridon-2-imine Hydrochloride</u>. Into a distillation flask was put 5.75 g of 1-(methylcarbamoyl)pyridon-2-imine hydrochloride and it was heated on a boiling-water bath. In a trap cooled with ice was collected 1.2 ml (70%) of methyl isocyanate (identified by its IR spectrum). To the residue to be recrystallized in the flask was added 30 ml of a 1 N NaHCO₃ solution, it was extracted with ether, and the ether extracts were dried over Na₂SO₄. After distilling the solvent off and subliming the residue, 2.35 g (60%) of 2-aminopyridine (identified by its IR and PMR spectra) was obtained.

<u>Reaction of 1-(Methylcarbamoyl)pyridon-2-(benzyl)imine with MeOH.</u> From 9.0 g of chelate (IIIe) was obtained 6.5 g (86%) of salt (IV) ($\mathbb{R}^2 = C_6H_5CH_2$, $\mathbb{R}^3 = H$, $\mathbb{R}^4 = Me$) and it was boiled for 3 h with 5 ml of abs. MeOH. Methyl N-methylcarbamate, bp 70-80°C (20 mm), n_D^{20} 1.4275 (see [17]), 1.2 g (52%), was isolated by distillation. The remainder was treated with 1 N NaHCO₃, the residue was filtered off and recrystallized from i-PrOH. 2-Benzylaminopyridine, mp 95-96°C (see [18]), 3.2 g (78%) was obtained.

<u>Dibutylboryl-[1-(allylthiocarbamoyl)pyridon-2-iminate] (V)</u>. To a solution of 9.7 g of 2-pyridylaminodibutylborane in 20 ml of abs. hexane was added 4.5 ml of allyl isothiocyanate (mild heating was observed). The hexane was distilled off within 2 days; the residue began to crystallize upon cooling. It was filtered off and washed with cold hexane. Chelate (V), mp 67-69°C, 12.56 g (89%), was obtained. Found: C 64.25; H 8.96; B 3.50; N 13.41; S 10.07%. $C_{17}H_{28}BN_3S$. Calculated: C 64.35; H 8.89; B 3.41; N 13.24; S 10.11%. IR spectrum (in CCl₄, ν , cm⁻¹): 1660 (C=N), 3412 (NH).

CONCLUSIONS

1. New chelate boron compounds with 1-carbamoylpyridon-2-imines and 1-thiocarbamoylpyridon-2imines as the ligands were obtained by adding 2-pyridylaminoboranes to isocyanates and isothiocyanates.

2. A method of synthesizing 1-carbamoylpyridon-2-imine hydrochlorides from 2-aminopyridine and isocyanates through the chelate boron compounds was proposed.

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SOME CHARACTERISTICS OF SILVLATING 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 silvlation of bis-o-aminophenols and the polycondensation in which their silvlated derivatives have participated, it became of interest to study these processes in more detail on model compounds. In connection with this the silvlation of o-, m-, and p-aminophenols with trimethylsilvldiethylamine and the conversion of their silvlation products were investigated in this paper.

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

$$HOC_{e}H_{a}NH_{s} + Me_{s}SiNEt_{s} \rightarrow Me_{s}SiOC_{e}H_{a}NH_{s} + HNEt_{s}$$
 (1)

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

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

$$Me_{3}SiOC_{6}H_{4}NH_{2} + Me_{3}SiNEt_{2} \rightarrow Me_{3}SiOC_{6}H_{4}NHSiMe_{3} + HNEt_{2}$$
(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

$$Me_{3}SiOC_{6}H_{4}NH_{2} - \underbrace{\stackrel{2EtMgBr}{-2C_{r}H_{6}}Me_{3}SiOC_{6}H_{4}N(MgBr)_{2} \xrightarrow{\frac{2Me_{3}SiOI}{-2MgBrC1}}Me_{3}SiOC_{6}H_{4}N(SiMe_{3})_{2}}_{-2MgBrC1} (4)$$

$$\underbrace{EtMgBr}_{-C_{6}H_{4}}Me_{3}SiOC_{6}H_{4}NH(MgBr) \xrightarrow{\frac{Me_{4}SiOI}{-2MgBrC1}}Me_{3}SiOC_{6}H_{4}NHSiMe_{3}}_{-MgBrC1} (4)$$

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

$$Me_{3}SiOC_{6}H_{4}NHSiMe_{3} + HOC_{6}H_{4}NH_{2} \rightarrow 2Me_{3}SiOC_{6}H_{4}NH_{2}$$
(3)

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