ORGANOBORON COMPOUNDS.

361. BORON CHELATE COMPOUNDS FROM N-(PYRID-2-YL)UREAS

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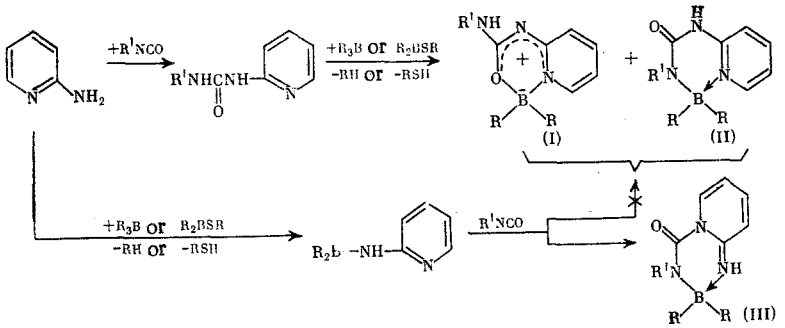
The present work is devoted to the chelates of boron with 2-carbamoylaminopyridines as the chelate-forming ligands. We have found that this type of compound may be obtained directly by the action of N-substituted N'-(pyrid-2-yl)ureas on organoboron compounds [1]. It appeared that the same chelates may be synthesized by the reaction of 2-pyridylaminoboranes with isocyanates. However, in fact, chelate compounds with 1-carbamoylpyridon-2-imines as the ligands were obtained [2]. Thus, it was possible to prepare three types of isomeric boron-containing chelates from 2-aminopyridine and isocyanates: carbamoylaminopyridinates (I) and (II) and carbamoylpyridoniminates (III):



In isomeric compounds (I) and (II), chelation is accomplished by the same ligand, namely, 2-alkylcarbamoylaminopyridine (or the 2-aryl analog), but in different fashion. Depending on the atom of the carbamoyl group to which the boron atom is bonded, we may term chelates (I) O-isomers and chelates (II) N-isomers. Compounds (I) and (II) differ in their chemical and physicochemical properties from chelates (III). Handschoe et al. [3] undoubtedly assigned the incorrect structure for the chelate N-diphenylboryl-N'-(pyrid-2-yl)ureas, i.e., chelates (II) to the products of the addition of 2-pyridylaminodiphenylborane to isocyanates.

The reaction of N-aryl-N'-(pyrid-2-yl)ureas with butylmercaptodiphenylborane proceeds smoothly in THF at ~20°C and yields a mixture of crystalline chelates (I) and (II). O-Diphenylboryl-[2-(arylcarbamoyl)-aminopyridinates] (Ia, b) (Table 1) are soluble in THF in contrast to their N-diphenylboryl isomers (IIa, b) and it was thus possible to separate (I) from (II).

Similarly, the action of N-aryl-N'-(pyrid-2-yl)ureas on butylmercaptobutylborane in THF or tributylborane in refluxing toluene yielded a mixture of chelates (I) and (II). Crystalline compounds (Ic) and (IIc and d) were isolated in pure form from the mixture as a consequence of the better solubility of isomers (I) in hexane [compound (Id) was isolated as a viscous, syrupy mass containing impurities]. It should be noted that isomeric chelates (I) and (II) are formed in approximately equal amounts in the reaction of N-aryl-N'-(pyrid-2-yl)-ureas and organoboranes. In contrast, N-methyl-N'-(pyrid-2-yl)urea yielded only chelate (IIe), while the O-isomer was not detected.

Carbamoylaminopyridinates (I) and (II) are relatively stable in the air and are not decomposed by water and alcohols. The structure of (I) and (II) was confirmed by IR, UV, ^{1}H NMR, ^{11}B NMR, and mass spectroscopy. The ^{11}B NMR spectra of all the compounds obtained have signals in the area of tetracoordinated boron. The mass spectra of (I) and (II) show an in-

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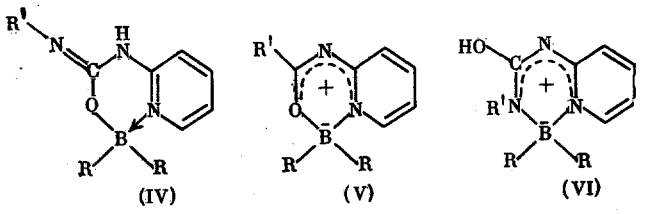
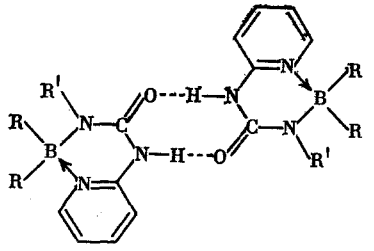
tense $(M - R)^+$ ion peak typical for boron chelates [4]. The major difference in the mass spectra of the isomers lies in the significantly greater loss of the RBO fragment from the $(M - R)^+$ ion for (I) relative to (II) (the mass spectroscopic study of the carbamoylaminopyridinates will be published separately). Valuable information on the structure of chelates (I) and (II) is provided by the IR spectra. The carbonyl band is lacking in the spectra of the O-isomers (I) in contrast to the N-isomers (II). On the other hand, an intense band at 1400-1500 cm^{-1} is observed in the case of (I) which should be assigned to the highly delocalized double-bond system. Neither the N-isomer (II) nor alternative structure for the O-isomer (IV) has a similar system. In the spectra of dialkylboryl(2-acylaminopyridinates) (V) [5] which have a structure similar to (I), the most intense bands are also observed at 1400-1500 cm^{-1}.



(IV) (V) (VI)

In the crystalline state, (I) molecules are associated due to intermolecular hydrogen bonding, but in CCl_4 solution, the NH group absorption is observed as a thin band at 3440 cm^{-1}.

The spectra of the N-isomers (II) have a strong band at 1670 cm^{-1} (νCO) both in the crystalline state and in solution. Thus, the alternative structure (VI) with a delocalized π-electron system is excluded. An interesting property of (II) is its high tendency to form associated species; in the crystalline state and even in highly dilute solutions, chelates (II) are dimerized due to the formation of NH bonds.



Thus, in the spectra of dilute solutions of (IIe) in CCl_4 even for conc. < 0.0003 M, absorption of bound C=O (1675 cm^{-1}) and NH (series of bands in the region 2600-3250 cm^{-1}) is observed. The dimer partially dissociates only upon heating with the appearance of the free CO groups (1695 cm^{-1}) and NH groups (3445 cm^{-1}), but the original spectrum is reproduced upon cooling of the solution to the initial temperature. Dimer decomposition partially proceeds also in acid and basic solvents. For example, a free NH group (3438 cm^{-1}) is observed in solutions of (IIc) and (IId) in $CHCl_3$ (especially upon the addition of a strong acid such as decachloroborane), while in THF, the free CO group band is observed at 1690 cm^{-1}. In benzene solution, compound (IId) is predominantly dimerized, which is also supported by the cryoscopic molecular weight determination of this compound. Finally, the NH signal is observed in the PMR spectra of (II) at very low field (~11 ppm), which also indicates strong hydrogen bonding. Such a marked capacity of compounds (II) to form associated species is a result of their cyclic structure with the NHCO fragment (for example, compare with 2-pyridone [6]) and donor–acceptor N → B bond. The effect of this donor–acceptor bond is manifested in the polarization of the remaining bonds in the ring and leads in the final analysis to an enhancement of the proton-donor properties of the NH group and proton-acceptor properties of the CO group (compare with the chelate derivatives hydroxy-, alkoxy-, and acyloxyboranes [7, 8]). We have previously noted the tendency for dimer formation with hydrogen bridging in the case of dibutylboryl(2-carboxyaminopyridinate) having a structure similar to (II) [9].

There are also significant differences in the UV spectra of chelates (I) and (II): the O-isomers (I) absorb at higher wavelengths than (II). Thus, the intense absorption bands for (Ic) characteristic of the conjugated system have maxima at 273 and 340 nm, which the corresponding bands for the N-isomer (IIc) have maxima at 202 and 248 nm; these bands are observed at

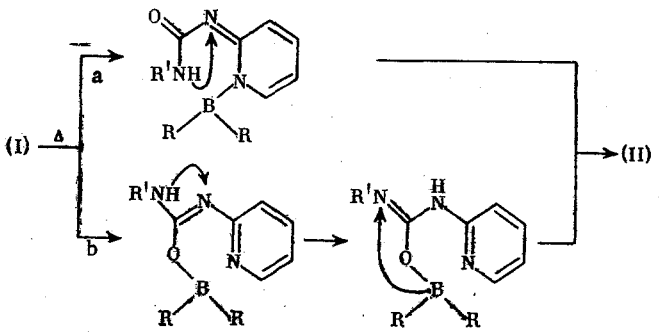
TABLE 1. Boron 2-Carbamoylaminopyridinates

Compound	R	R′	mp, °C	^{11}Br NMR in THF, chemical shift, ppm	Found, %				Empirical formula	Calculated, %			
					C	H	B	N		C	H	B	N
(Ia)	Ph	Ph	*	−4,5±1	76,67	5,33	2,95	11,16	$C_{24}H_{20}BN_3O$	76,41	5,34	2,87	11,14
(IIa)	Ph	Ph	264–265	†	76,53	5,50	3,03	11,34					
(Ib)	Ph	o-MeC_6H_4	*	−4,5±1	76,69	5,71	2,78	10,65	$C_{25}H_{22}BN_3O$	76,74	5,67	2,76	10,74
(IIb)	Ph	o-MeC_6H_4	244–247	†	76,94	5,73	2,88	10,80					
(Ic)	Bu	o-MeC_6H_4	80–81	−9,0±2	71,87	8,69	3,15	11,79	$C_{21}H_{30}BN_3O$	71,80	8,61	3,08	11,96
(IIc)	Bu	o-MeC_6H_4	162–166	−7,0±2	72,28	8,69	3,32	11,90					
(IId)	Bu	Ph	143–146 ‡	−6,0±2	71,36	8,44	3,34	–	$C_{20}H_{28}BN_3O$	71,22	8,37	3,21	12,40
(IIe)	Bu	Me	165–168 **	−4,0±1	65,34	9,41	4,00	14,77	$C_{15}H_{26}BN_3O$	65,52	9,53	3,94	15,22

*Converts to isomer (II) without melting.
†The solubility of this compound in THF is low.
‡From heptane.
**From hexane.

~200 and 250 nm for N-(o-tolyl)-N'-(pyrid-2-yl)urea. The sharp difference in the spectra of (I) from (II) and the starting urea is apparently the result of a more extensive conjugated system in (I). It is interesting that dibutylboryl[1-(o-tolylcarbomoyl)pyridon-2-iminate] (III, R = Bu, o-MeC_6H_4), which is isomeric to compounds (Ic) and (IIc), absorbs at <200 nm (ε > 30,000), 254 nm (ε 9600), and 364 nm (ε 1800). The spectral similarity of this chelate and (IIc) is understandable since the difference in their structures lies only in the presence of the pyridonimine fragment instead of the aminopyridine fragment.

A study of the thermal stability of the boron carbamoylaminopyridinates showed that chelates (I) upon heating are capable of isomerization to (II). Thus, O-isomer (Ia) is converted completely into the N-isomer (IIa) at 180-190°C for 6 h. The transformation of (Ib) to (IIb) is even more facile and requires heating at 150-180°C for 1 h. It may be proposed that the conditions for this unique intrachelate rearrangement, in general, depend on the strength of the coordination of boron with the ligand in (I). Indeed, the chelates with the dialkylboryl group isomerize more readily than chelates with the diphenylboryl group (for the same ligand), since the acceptor capacity of boron is low in the former. For example, (IIc) is formed easily from (Ic) even at 135°C. This rearrangement likely proceeds with opening of the chelate ring and subsequent 1,3-(N → N) migration of the hydrogen atom (path *a* in the scheme). The isomerization may also involve 1,3 migration of the R_2B group (path b).



The thermal isomerization of (I) into (II) may be used for increasing the yield of (II) in the preparation from N-aryl-N'-(pyrid-2-yl)ureas and organoboranes. For example, chelate (IId) was obtained in 72% yield from the corresponding urea and tributylborane upon heating a crude mixture of O- and N-isomers at 140-145°C.

EXPERIMENTAL

The operations were carried out in dry nitrogen. The starting N-aryl-N'-(pyrid-2-yl)-ureas and N-methyl-N'-(pyrid-2-yl)urea were prepared by a known method from 2-aminopyridine and isocyanates.

The ^{11}B NMR spectra were taken on RS-56/19 and Bruker SXP4-100 spectrometers. The PMR spectra were taken on a Varian 60-IL spectrometer. The IR spectra were taken on a UR-20 spectrometer. The UV spectra were taken in ethanol on a Specord UV-VIS spectrometer. The mass spectra were taken on a Varian MAT CH-6 mass spectrometer.

O- and N-Diphenylboryl(arylcarbamoylaminopyridinates) (Ia, b) and (IIa, b). To 0.02-0.03 mole butylmercaptodiphenylborane, either a solution or suspension of 0.015-0.02 mole N-aryl-N'-(pyrid-2-yl)urea in 100 ml abs. THF was added and stirred for 6-8 h. The crystals formed were filtered off, washed with abs. THF, and (IIa, b) was obtained (Table 2). The filtrate was evaporated to dryness, treated with abs. toluene, and filtered to separate (Ia, b).

O- and N-Dibutylboryl(2-arylcarbamoylaminopyridinates) (Ic, d) and (IIc, d) from Butylmercaptodibutylborane. The preparation was carried out similarly to the previous synthesis. After distilling off THF and other volatile components in vacuum, 15-20 ml cold abs. hexane was added, filtered and (IIc) and (IId) were separated on the filter. Hexane was evaporated from the filtrate. Crystalline (Ic) and syrupy (Id) containing impurities were obtained.

Preparation of (Ic, d) and (IIc, d) from Tributylborane. A mixture of 0.07-0.08 mole tributylborane and 0.045-0.05 mole of the corresponding N-aryl-N'-(pyrid-2-yl)urea in 40-50 ml abs. toluene was heated at reflux until the cessation of gas liberation (2-3 h). Toluene and ex-

TABLE 2. Reactions of N-Aryl-N'-(pyrid-2-yl)-ureas and N-Methyl-N'-(pyrid-2-yl)urea with Organoboranes

Starting compounds		Reaction products, yield, %
organoboron compound	R' in R'NHCONH(C_5H_4N-α)	
Ph_2BSBu	Ph	(Ia), 60; (IIa), 37
Ph_2BSBu	o-MeC_6H_4	(Ib), 51; (IIb), 44
Bu_2BSBu	o-MeC_6H_4	(Ic), 48; (IIc), 42
Bu_3B	o-MeC_6H_4	(Ic), 37; (IIc), 52
Bu_2BSBu	Ph	(Id) * (IId), 54
Bu_3B	Ph	(Id) * (IId), 40†
Bu_2BSBu	Me	(IIe), 91
Bu_3B	Me	(IIe), 90

*Not isolated in pure form.
†(IId) was obtained in 72% yield in the run in which the reaction mixture was heated for 1 h at 145-155°C and the solvent distilled off.

cess tributylborane were distilled off in vacuum with heating over a water bath and then the residue was treated as in the preceding experiment. (In some runs, the residue was heated in a flask at 140-150°C for 1-3 h prior to treatment in order to increase the yield of (IIc) and (IId).) The PMR spectrum of (Ic) in $CDCl_3$ (δ, ppm): 8.43 br. s (NH), 6.38-7.77 m (aromat. protons), 2.24 s (Me), 0.22-1.48 m (2Bu). PMR spectrum of (IIc) in $CDCl_3$: 11.09 br. s (NH), 6.56-7.88 (aromat. protons), 2.16 s (Me), 0.25-1.45 m (2Bu). UV spectrum of (Ic) (λ, nm (ε)): < 200 (>30,000), 273 (26,700), 340 (17,000). UV spectrum of (IIc): 202 (31,500), 248 (15,900), 315 (3190).

Dibutylboryl(2-methylcarbamoylaminopyridinate) (IIe). Compound (IIe) was obtained from N-methyl-N'-(pyrid-2-yl)urea and tributylborane (or butylmercaptodibutylborane) analogously to (IIc) and (IId). The corresponding isomer (Ie) was not observed in the reaction products. PMR spectrum of (IIe) in $CDCl_3$ (δ, ppm): 11.65 s (NH), 7.45-7.90 m [H(4) and H(6) of the pyridine ring], 6.71-7.15 m [H(3) and H(5)], 2.80 s (MeN), 0.23-1.57 m (2Bu). UV spectrum [λ, nm (ε)]: 201 (19,500), 254 (9600), 321 (3800).

Thermal Isomerization of (Ia-d) into (IIa-d). A sample of 1 g (Ia) or (Ib) was placed in a flask and heated on an oil bath at 150-190°C. The conversion to (IIa) and (IIb) was monitored by IR spectroscopy. The isomerization of (Ic) and (Id) to (IIc) and (IId) was carried out analogously at 135-150°C.

CONCLUSIONS

1. Isomeric chelate compounds, namely O- and N-di-R-(2-carbamoylaminopyridinates) (R = alkyl or aryl) were synthesized from N-alkyl(or aryl)-N'-pyrid-2-yl)ureas and organoboranes.

2. The capacity of O-di-R-boryl(2-carbamoylaminopyridinates) (R = alkyl or aryl) to undergo thermal rearrangement to N-di-R-boryl(2-carbamoylaminopyridinates) was discovered.

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REACTION OF TETRACYCLONE WITH THE ETHYL ESTER OF PHENYLPHOSPHONOUS ACID

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Earlier it was shown that the methyl ester of phenylphosphonous acid reacts with tetracyclone (TC) in the absence of a catalyst according to the scheme of 1,4- and 1,6-addition [1], while in the presence of a base it proceeds only by 1,6-addition [2]. Unlike dimethyl phosphite [3-5], the addition products are not formed at the carbonyl group.

Ethyl phenylphosphonite in the presence of triethylamine (TEA) easily and quantitatively forms a 1,2-addition with TC, i.e., the ethyl ester of 1-hydroxy-2,3,4,5-tetraphenylcyclopenta-2,4-dienyl-1-phenylphosphinic acid (I), the constants and spectral characteristics of which are presented in Table 1. The shift of $\nu_{P=O}$ and ν_{OH} bands in the IR spectra to the region of lower frequencies indicates a H bond between P=O and OH groups.

Similar to α-hydroxyphosphonate from dimethyl phosphite [3, 4], α-hydroxyphosphinate (I) in a reaction mixture in the presence of TEA is gradually converted to a mixture of phosphonenol (II) and nonconjugated β-ketophosphinate (III). In its course, (III) is isomerized to a mixture of conjugated ketophosphinates which are separated by chromatographing on silica gel. On the basis of the IR and PMR spectral data, in agreement with [1, 2], the structure of conjugated β-ketophosphinates with cis-(V) and trans-(VI) positions of the methyl proton and the phosphono group is assigned to the products obtained. Both diastereoisomers (Va) and (Vb) (Tables 1 and 2) are isolated in crystalline form for the cis isomer. The uncrystallized trans isomer also is a mixture of diastereoisomers. In the reaction the trans isomer is formed preferentially and its amount surpasses the amount of the cis isomer (V). In contrast to [3, 4], the conversion of α-hydroxyphosphinate (I) to enolphosphonate (IV) was not observed.

With the goal of explaining the path of the conversion of (I) to (III) in the presence of a base (intramolecular rearrangement or decomposition to the original components), the behavior of (I) in the presence of TEA and a fourfold excess of competing acid, methyl phenylphosphonite, was studied. After chromatographing the reaction mixture, conjugated ketophosphinates (V) and (VI) with ethoxy groups were isolated. According to PMR spectral data, small amounts of β-ketophosphinates with MeO groups on the phosphorus are also formed. This indicates that α-hydroxyphosphinate (I) under conditions of basic catalysis can be converted into β-ketophosphinate both intramolecularly and also intermolecularly through decomposition to the original components, but the process of intramolecular isomerization predominates.

Upon conducting the reaction of TC with ethyl phenylphosphonite in the presence of equimolar amounts of diethylamine or morpholine, as also in the case of methyl phenylphosphonite [2], α-hydroxyphosphinate (I) does not form, but ammonium salts (IXa) and (IXb) do. This is explained by the fact that α-hydroxyphosphinate (I) during action with secondary amines is quickly converted into salts (IXa) and (IXb). These same salts are formed during reaction of amines on ketone (III). The enol (II) (see Table 1) is obtained upon treatment of the ammonium salts (IXa) and (IXb) with AcCl. The location and character of absorption bands $\nu_{P=O}$ and ν_{OH} of (II) indicate a H bond between the P=O and OH groups.

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