Journal of Organometallic Chemistry, 238 (1982) 159—170
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PREPARATION AND STUDY OF CHIRAL BORON CONTAINING AMINE-CYANO(PYRROLYL-1)BORANE COMPLEXES. PREPARATION OF (—)-(*S*)-α-PHENYLETHYLAMINE-(—)-CYANO(PYRROLYL-1)BORANE AND (+)-(*R*)-α-PHENYLETHYLAMINE-(+)-CYANO(PYRROLYL-1)BORANE

BÉLA GYŐRI and JÓZSEF EMRI

Department of Inorganic and Analytical Chemistry, L. Kossuth University, H-4010 Debrecen (Hungary)

(Received May 5th, 1982)

Summary

Several amine-cyano(pyrrolyl)borane complexes [A · $BH(NC_4H_4)CN$] containing a chiral boron atom were prepared from the reactions of sodium cyanohydrodipyrrolylborate-tridioxane * [$NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2$] with amine hydrochlorides as well as by base exchange from the appropriate 4-cyanopyridine complex [$4\text{-}CNC_5H_4N \cdot BH(NC_4H_4)CN$]. Amines with an sp^2 N atom give stable complexes of a wide range of basicity (pK_a = 0.8—9.7), in contrast to the amines with sp^3 hybridized N where only the stronger bases ($pK_a > 7.3$) are capable of giving stable complexes (mainly secondary and tertiary amines). These compounds undergo hydrolysis in neutral and alkaline media, while in strong acids they give stable boronium ions by protonation at the α-C atom of the pyrrolyl group. The compounds (—)-(*S*)-α-phenylethylamine-(—)-cyanopyrrolylborane and (+)-(*R*)-α-phenylethylamine-(+)-cyanopyrrolylborane have been prepared in pure form; in solution they undergo slow epimerization. Treatment of the appropriate complexes with KH has given the chiral boron-containing borates $KBH(NC_4H_4)(CN)X$ (X = imidazolyl-, pyrazolyl-). Dicyanohydropyrrolylborane was obtained from 4-cyanopyridine-cyanopyrrolylborane and NaCN.

Introduction

We previously described the preparation and study of chiral boron containing pyridine- and 4-picoline-cyanopyrrolylborane complexes [1]. The existence of the two enantiomers of the 4-picoline complex was demonstrated by ^1H

* In this paper "pyrrolyl" means pyrrolyl-1 throughout.

0022-328X/82/0000—0000/$02.75

NMR spectroscopy and it was shown that their interconversion, if any, is slow on the NMR time scale. Continuing our study of the preparation of chiral boron-containing compounds (only a few of which are known [1—4]) we have investigated the reaction conditions for the preparation of the $A \cdot BH(NC_4H_4)CN$ (A = amine) complexes from $NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2$ by treatment with amine hydrochlorides as well as from $4\text{-}CNC_5H_4N \cdot BH(NC_4H_4)CN$ through base exchange.

Results and discussion

The reaction between $NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2$ and the hydrochlorides of sp^2-hybridized *N*-bases gives cyanopyrrolylborane (with a few exceptions) when the pK_a values of the bases are between 0.8 and 8 and the reaction is conducted in THF at room temperature:

$$NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2 + A \cdot HCl \xrightarrow[\text{room temp.}]{\text{THF}} A \cdot BH(NC_4H_4)CN + NaCl + C_4H_4NH + 3C_4H_8O_2 \quad (1)$$

(A (in the order of decreasing pK_a values) = 2-aminopyridine (I) *, 4-picoline (II), benzimidazole (III), 1-(4-pyridyl)ethanol (IV), pyridine (V), 4-chloropyridine (VI), isonicotinic acid methyl ester (VII), pyrazole (VIII), 3-cyanopyridine (IX), 4-cyanopyridine (X), 3,5-dichloropyridine (XI))

In the case of imidazole hydrochloride the main product (~66%) is the dipyrrolylborane complex $C_3H_4N_2 \cdot BH(NC_4H_4)_2$ (XIIb), along with ~21% of $C_3H_4N_2 \cdot BH(NC_4H_4)CN$ (XIIa):

$$NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2 + C_3H_4N_2 \cdot HCl \xrightarrow[\text{room temp.}]{\text{THF}} C_3H_4N_2 \cdot BH(NC_4H_4)_2 + NaCl + HCN + 3C_4H_8O_2 \quad (2)$$

When 4,4′-dipyridyl was employed in a 2/1 borate to base dihydrochloride ratio, 4,4′-dipyridyl-bis(cyanopyrrolylborane) $[C_{10}H_8N_2 \cdot 2BH(NC_4H_4)CN]$ (XIIIa), containing two chiral boron atoms, was formed. Of the bases with sp^2-hybridized N, only the sterically hindered 2,4,6-collidine, acridine and 2,2′-dipyridyl did not yield the expected complexes.

In sharp contrast, of the sp^3 *N*-containing amines of similar basicity the only complex we could isolate from reaction 1 was the bis(chloroethyl)amine-cyanopyrrolylborane $[(ClCH_2CH_2)_2NH \cdot BH(NC_4H_4)CN]$ (XIV). Amine hydrochlorides belonging to this group underwent reactions in several instances but none of the expected complexes or other homogeneous substances could be isolated. The following amines were tried: *N*,*N*-diethylaniline, *p*-phenylenediamine, methyl(cyanomethyl)amine, *N*,*N*-dimethylaniline, 4-chloroaniline, 2,4-dichloroaniline and diphenylamine.

With strongly basic ($pK_a > 8$) amines displacement took place at room tem-

* The roman numerals refer to the amineboron compound and not to the amine itself.

perature independent of the character of the amine:

$$NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2 + A \cdot HCl \xrightarrow[\text{room temp.}]{THF} AH^+BH(NC_4H_4)_2CN^- + NaCl + 3C_4H_8O_2 \quad (3)$$

(A = 4-dimethylaminopyridine (XV), 4-aminopyridine (XVI), piperidine (XVII), quinuclidine (XVIII), methylamine (XIX), trimethylamine (XX), allylamine (XXI), racemic α-phenylethylamine (XXII), morpholine (XXIII))

From the hydrochlorides of the moderately strong ($pK_a \approx 7$) bases 2-aminopyridine and imidazole the salts (2-aminopyridinium cyanohydrodipyrrolylborate (XXIV) and imidazolium cyanohydrodipyrrolylborate (XXV)) were obtained in CH_3CN at room temperature instead of the complexes.

The thermal stability of the ammonium cyanohydrodipyrrolylborates is low for the quinuclidinium salt. They decompose within 0.5 h (2 h in the case of the 4-aminopyridinium salt) when refluxed in THF solution. During the decomposition of XX and XXII amine-cyanopyrrolylboranes are formed:

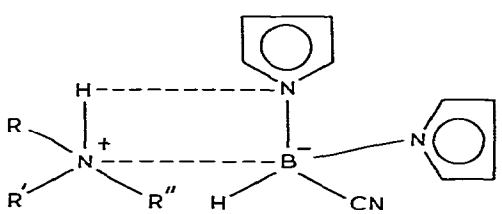
$$AH^+BH(NC_4H_4)_2CN^- \xrightarrow[\text{reflux, 0.5 h}]{THF} A \cdot BH(NC_4H_4)CN + C_4H_4NH \quad (4)$$

(A = racemic α-phenylethylamine (XXVIa), trimethylamine (XXVII))

It was not possible to get homogeneous products from the methylammonium, allylammonium and piperidinium salts, but the morpholinium salt gave morpholine-dipyrrolylborane (XXVIII) in low yield.

The decomposition of two salts (XV, XVI) containing an sp^2-hybridized N atom yields dipyrrolylborane complex as the main product and a smaller amount of cyanopyrrolylborane complex. The following amounts were found: ~27% 4-aminopyridine-cyanopyrrolylborane (XXIXa) and ~64% 4-aminopyridine-dipyrrolylborane (XXIXb) in the case of XVI, and ~17% 4-dimethylaminopyridine-cyanopyrrolylborane (XXXa) and ~78% 4-dimethylaminopyridine-dipyrrolylborane (XXXb) in the case of XV.

In contrast to all other salts, the quinuclidinium salt decomposes only to a small extent (max. 15—20%) even after 7 h boiling in THF. This observation permits us to assume that the formation of the amine-boranes from ammonium cyanohydrodipyrrolylborates goes through a four-center intermediate shown below the formation of which is sterically hindered in the case of the quinuclidinium salt:



We made several amine-cyanopyrrolylboranes by base displacement in ether using the very weak base 4-cyanopyridine complex:

$$4\text{-}CNC_5H_4N \cdot BH(NC_4H_4)CN + A \xrightarrow{Et_2O} A \cdot BH(NC_4H_4)CN + 4\text{-}CNC_5H_4N \quad (5)$$

A = 4-dimethylaminopyridine (XXXa), 4-aminopyridine (XXIXa), imidazole (XIIa), 2-aminopyridine (I), 4,4′-dipyridyl (XIIIb), piperidine (XXXI), quinuclidine (XXXII), dimethylamine (XXXIII), s-butylamine (XXXIV), racemic α-phenylethylamine (XXVIa) (—)-(*S*)-α-phenylethylamine (XXVIb), (+)-(*R*)-α-phenylethylamine (XXVIc).

We prepared 4,4′-dipyridyl-bis(cyanopyrrolylborane) (XIIIa) and bis(4,4′-dipyridyl)-cyanopyrrolylborane (XIIIc) via base exchange with 4,4′-dipyridyl. Base exchange took place but no characterizable or solid product could be obtained with NH_3 or several primary amines (methylamine, *L*-2-amino-1-butanol, allylamine, (4-pyridyl)-methylamine, benzylamine, methyl(cyanomethyl)amine, aniline) or with the secondary amine morpholine. No reaction occurred with diethylaniline.

The results show that the cyanopyrrolylborane gives complexes more readily with sp^2 *N*-containing amines than with sp^3 amines. Stable complexes were obtained even with very weakly basic amines towards protons (pK_a up to 0.8). In contrast, no complex formation was detected with sp^3 amines which were weaker bases than bis(chloroethyl)amine ($pK_a \approx 7.3$). Secondary and tertiary amines which are stronger sp^3 bases than the bis(chloroethyl)amine give stable complexes (with the exception of morpholine) while the majority of primary amines and ammonia yield no stable complexes. Only two of the primary amines (s-butylamine and α-phenylethylamine) give stable complexes, and in both of these the NH_2 group is attached to a tertiary carbon atom.

The enhanced basicity of the sp^2 amines with respect to the $BH(NC_4H_4)CN$ borane is reflected in the equilibrium constant which was measured spectrophotometrically in THF:

$$4\text{-}CNC_5H_4N \cdot BH(NC_4H_4)CN + (ClCH_2CH_2)_2NH \overset{THF}{\rightleftharpoons} (ClCH_2CH_2)_2NH \cdot BH(NC_4H_4)CN + 4\text{-}CNC_5H_4N; \quad K = 0.239 \pm 0.033 \quad (6)$$

The analogous *K* value calculated for the distribution of the proton between the two bases in water is 9.5×10^5. These data show that the cyanopyrrolylborane is, like borane [5], a soft or border line Lewis acid.

The amine complexes of cyanopyrrolylborane are slightly soluble in water, and undergo hydrolysis in water and in water-organic solvent mixtures in the weakly acidic, neutral and alkaline range. Their hydrolysis is similar to that of the amine-cyanoboranes ($A \cdot BH_2CN$) [6]. This is confirmed by the data in Table 1, which shows the approximate hydrolytic half-lives of complexes of various types.

The complexes show good solubility in concentrated mineral acids and the solubility increases with increasing acid concentration. The ultraviolet absorption spectra in more concentrated (>50%) H_2SO_4 solution show an absorption maximum at 245 nm and are reminiscent of the spectrum of pyrrole in conc. H_2SO_4 [7]. The ^1H NMR spectra of the concentrated H_2SO_4 or HCl solutions show (again like pyrrole [8]) a two-proton intensity resonance at δ 5.05 ppm. These observations clearly indicate that in more concentrated acids protonation takes place at the α-carbon of the pyrrole ring with concomitant formation of $A \cdot BH(NC_4H_5)CN^+$ boronium ions. The protonation occurs at acid concentrations similar to those found with pyrrole and 1-methylpyrrole. The H_2SO_4 con-

TABLE 1

APPROXIMATE HYDROLYSIS HALF-LIVES OF SOME A · $BH(NC_4H_4)CN$ COMPLEXES DETERMINED SPECTROPHOTOMETRICALLY IN 0.025 *M* H_2SO_4 (a), 0.025 *M* BORAX (b) AND 0.05 *M* NaOH SOLUTION IN THE PRESENCE OF 2% OF METHYL CYANIDE AT ROOM TEMPERATURE

A	Half-life (min)		
	a	b	c
pyridine	1900	1800	1900
4-cyanopyridine	5.7	5.7	1.2
(—)-(*S*)-α-phenylethylamine	very long	2.9	0.08
piperidine	very long	2700	1.3
bis(chloroethyl)amine	130	7.2 [a]	0.08

[a] In phosphate buffer (pH = 7.2).

centration values corresponding to the half-protonation point are around 3.2—3.6 *M*.

To explain the possibility of obtaining aminoborates with a chiral boron atom we undertook a study of the reaction between alkali metal hydrides and several complexes containing N—H bonds. The appropriate amino-borates could only be obtained with KH from the imidazole and the pyrazole complexes: in both cases the hydrogen eliminated was that attached to an N atom rather than that bonded to boron:

$$C_3H_4N_2 \cdot BH(NC_4H_4)CN + KH \xrightarrow{THF} KBH(C_3H_3N_2)(NC_4H_4)CN + H_2 \quad (7)$$

($C_3H_4N_2$ = imidazole, pyrazole)

The borates were isolated in the form of dioxane adducts (potassium cyanohydroimidazolylpyrrolylborate-1.5 dioxane (XXXV) and potassium cyanohydropyrazolylpyrrolylborate-1 dioxane (XXXVI).

As shown earlier, the 4-cyanopyridine can be exchanged for another amine (5 reactions) in the cyanopyrrolylborane complex. We have explored the possibility of exchange with Lewis base anions employing their alkali metal salts. No exchange was observed with LiH, LiCN, NaCN, $NaNH_2$, NaN_3, LiOMe, phenyllithium, n-butyllithium, cyclopentadienylsodium and pyrrolylpotassium using Et_2O, Me_2S, THF or dioxane as solvents. However, exchange took place with NaCN in the melt:

$$4\text{-}CNC_5H_4N \cdot BH(NC_4H_4)CN + NaCN \xrightarrow{100-110^\circ C} NaBH(NC_4H_4)(CN)_2 + 4\text{-}CNC_5H_4N \quad (8)$$

The sodium dicyanohydropyrrolylborate was obtained as a dioxane adduct ($NaBH(NC_4H_4)(CN)_2 \cdot 2C_4H_8O_2$, (XXXVII)); to the best of our knowledge this is the first dicyanoborate.

The methyl protons in the two diastereomeric cyanopyrrolylborane complexes obtained from racemic α-phenylethylamine show two well-separated resonances in their ^1H NMR spectrum (Fig. 1, a1). Two well-separated pairs of NH_2 signals can also be clearly distinguished. As the ^1H NMR spectrum shows

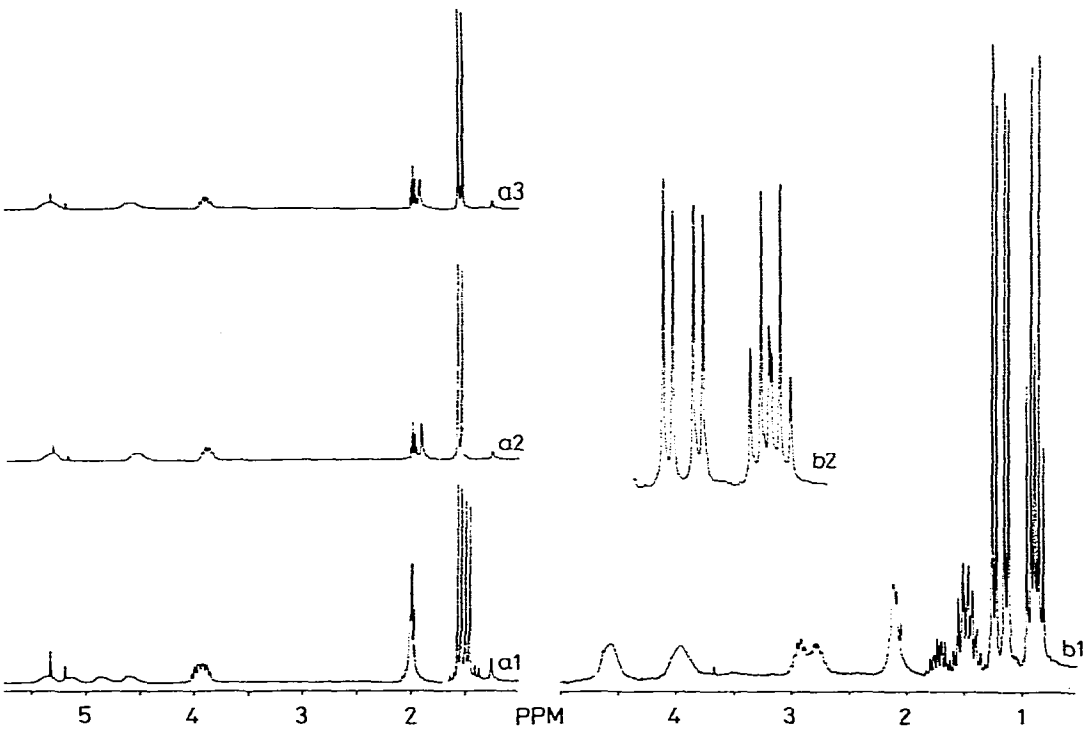


Fig. 1. ^{1}H NMR spectra of the α-phenylethylamine-cyanopyrrolylborane complexes (XXVIa: a1; XXVIb: a2; XXVIc: a3) in 94% $CDCl_3$-6% CD_3CN and of s-butylamine-cyanopyrrolylborane (XXXIV) in $CDCl_3$ (b1, b2).

the diastereoisomers are formed in an approximately 1/1 mixture. It formed an oil from which no solid could be obtained. When either (—)-(*S*)- or (+)-(*R*)-α-phenylethylamine is used, the product displays an ^{1}H NMR spectrum identical with a1 in Fig. 1, but one of the epimers crystallizes out from the purified chloroform solution of the mixture (Fig. 1, spectra a2 and a3). It can be assumed that a rapid epimerization takes place concurrently with the crystallization since all the complex in solution was isolated in this way. According to their ^{1}H NMR spectra compounds XXVIb and XXVIc obtained from (—)-(*S*)- and (+)-(*R*)-α-phenylethylamines, respectively, are enantiomers. This is confirmed by the specific optical rotation values $[\alpha]_D^{25}$: —62.1° for XXVIb and +63.9° for XXVIc (in dioxane). The absolute value of $[\alpha]_D^{25}$ slowly decreases in both cases. This can be ascribed to an epimerization process which is also confirmed by ^{1}H NMR spectroscopy. Based on the above, the structures of the two complexes are:

XXVIb: (—)-(*S*)-α-phenylethylamine-(—)-cyanopyrrolylborane;

XXVIc: (+)-(*R*)-α-phenylethylamine-(+)-cyanopyrrolylborane.

Studies in progress [9] indicate that the half-life of the epimerization varies between 20 to 100 h depending on the solvent and other factors. In contrast, the half-life for the epimerization of XXVIb and XXVIc during crystallization cannot exceed a few minutes. XXVIb and XXVIc may be utilized for reduction

of carbonyl groups under appropriate conditions. Investigations are under progress [9] to determine the enantioselectivity of such reactions in the case of prochiral carbonyl compounds.

The racemic s-butylamine-cyanopyrrolylborane was obtained as an oil, consisting of an approximately 1/1 mixture of the two diastereoisomers as indicated by the ^{1}H NMR spectrum b1/b2 in Fig. 1. Two sets of equal intensity signals are clearly shown for both the CH_3(4) (~0.8 ppm), CH_3(1) (~1.3 ppm) and NH_2 (~4 and ~4.6 ppm) groups, respectively. The diastereoisomers could not be separated in crystalline form.

Experimental

Reactions were conducted in dry, oxygen-free solvents under dry nitrogen. The sodium cyanohydrodipyrrolylborate-tridioxane was prepared by a published procedure [1], and the amine hydrochlorides were obtained from the amines in ether. The pK_a values were usually taken from the literature [10—12], but approximate values were calculated [13] in some cases.

The IR and UV spectra were recorded on Perkin—Elmer 283 and Beckman Acta MIV spectrophotometers, respectively. The ^{1}H NMR spectra were obtained on a Bruker WP 200 SY and a JEOL MH-100 spectrometer. Optical rotations were measured on a Perkin—Elmer model 241 polarimeter.

For the determination of hydrolysis half-lives the compounds were dissolved in CH_3CN, diluted with water to $2.5—5 \times 10^{-4}$ *M*. These solutions were diluted in 1/1 ratio with either 0.1 *M* NaOH, 0.05 *M* borax or 0.05 *M* H_2SO_4 solutions. The variation of the UV absorbance was monitored at 230 nm (for XIV, XXVIb and XXXI), 235 nm (for X) or 263 nm (for V). The UV absorbance value of the hydrolysis products was measured after eight half-lives. The half-lives were calculated from the graphically-determined pseudo first-order rate constants.

The boron content was determined acidalcalimetrically in the presence of mannitol after fusion with NaOH. For compounds XXXV—XXXVII the K and Na contents were measured in the presence of acetone by titration with 0.1 *M* HCl using methyl orange as indicator.

The physical, analytical and IR-spectroscopical data for all compounds are summarized in Table 2. Compounds IV, VII, XXVIa and XXXIV are colorless or pale yellow oils, X, XIIIa and XIIIb yellow crystalline solids, and the other compounds white crystalline solids.

A1. Reaction of $NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2$ with amine (pK_a < 8) hydrochlorides in THF at room temperature

A solution of $NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2$ (1.50 g, 3.28 mmol) in THF (10 ml) is added with stirring to a suspension of the amine hydrochloride (3.28 mmol) in THF (10 ml). The mixture is filtered after 10 min and the filtrate evaporated at room temperature either in a N_2 stream or under reduced pressure. Ether (15 ml) is added to the residue and the crystals thus obtained are filtered off. The crude product is purified by extraction with ether.

The crystallization after the addition of ether was complete only after 2—3 days in the case of I, and of the mixture of XIIa—XIIb, while 5—6 days were required in the case of IX. XIIb was obtained by extracting the crude product

TABLE 2

PREPARATIONS, YIELDS, ANALYTICAL AND IR DATA OF PRODUCTS

Compound	Method	Yield (%)	Analyses (Found (calcd.)(%))		IR data (cm^{-1})	
			B		ν(B—H)	ν(C≡N)
I	A1	15	5.33 (5.46)		2415	2220
	C1	72	5.41			
II	A1	70	5.56 (5.49)		2441	
III	A1	73	4.71 (4.87)		2409 2440sh	
IV	A1	58	4.55 (4.76)			
V	A1	71	5.80 (5.91)		2463	
VI	A1	52	5.05 (4.97)		2444	
VII	A1	47	4.20 (4.48)			
VIII	A1	78	6.24 (6.29)		2438	2223
IX	A1	34	5.38 (5.20)		2438, 2450,	2245
X	A1	66	5.31 (5.20)		2455	2240
XI	A1	32	4.03 (4.29)		2458	
XIIa	C1	59	6.20 (6.29)		2412, 2430	
XIIb	A1	31	5.22 (5.10)		2422, 2440	
XIIIa	A1	64	5.76 (5.94)		2443	
	C2	97	5.84		2444	
XIIIb	C2	82	4.11 (4.16)		2451	
XIIIc	C2	86	2.65 (2.60)		2408sh 2420	
XIV	A1	59	4.42 (4.40)		2462	
XV	A2	80	3.75 (3.69)		2398, 2418, 2433sh	2200
XVI	A2	78	3.98 (4.08)		2405, 2425, 2395sh	2193
XVII	A2	83	4.34 (4.22)		2406, 2421,	2199
XVIII	A2	88	3.86 (3.83)		2400, 2408, 2424	2192
XIX	A2	75	5.21 (5.35)		2388, 2416, 2425sh	2218
XX	A2	67	4.55 (4.70)		2360, 2396 2423	
XXI	A2	82	4.68 (4.74)		2404, 2423,	2218
XXII	A2	77	3.77 (3.70)		2403, 2418,	2221
XXIII	A2	84	4.22 (4.19)		2397, 2410, 2424	2202
XXIV	A3	33	4.17 (4.08)		2393, 2418,	2204
XXV	A3	52	4.70 (4.52)		2403, 2416, 2424	2203
XXVIa	B	40	4.59 (4.80)			
	C1	55	4.54			
XXVIb	D	52—63	4.75 (4.80)	}	2424,	2221
XXVIc	D	62	4.71 (4.80)	}	2437sh	
XXVII	B	61	6.84 (6.63)		2467	
XXVIII	B	31	4.79 (4.68)		2432, 2454	
XXIXa	C1	53	5.37 (5.46)		2442	
XXIXb	B	34	4.62 (4.54)		2388	
XXXa	C1	94	4.76 (4.78)		2440	
XXXb	B	47	4.15 (4.06)		2425br	
XXXI	C1	84	5.75 (5.72)		2448, 2420sh	2208
XXXII	C1	57	4.86 (5.03)		2452,	2219
XXXIII	C1	95	7.15 (7.25)		2422, 2404sh	2225
XXXIV	C1	32	5.97 (6.11)			
XXXV	E	88	3.07 (3.16)		2411, 2444,	2211
			K%	11.63 (11.42)		
XXXVI	E	59	3.62 (3.63)		2387, 2416,	2200
			K%	13.27 (13.11)		
XXXVII	F	46	3.41 (3.28)		2397, 2408,	2213
			Na%	7.14 (6.98)		

with ether (20 ml) 30 times. For III the crystallization took 5—15 h; in this case the product was the residue obtained after several extraction with ether. In the case of IV and VII the oils obtained after evaporation of the reaction mixture were dissolved in $CHCl_3$ (5 ml) and the solution was shaken with 0.5 *M* H_2SO_4 (2 × 5 ml); then washed with water, dried over A4 molecular sieve, evaporated, and kept under reduced pressure (0.01 mbar) for 0.5 h.

In the case of VIII, hexane was used in place of ether. The material obtained after filtration was extracted with the filtrate until it was no longer sticky, leaving the required product as the residue.

In the case of XI the product left after evaporation of the reaction mixture was dissolved in $CHCl_3$ (5 ml), and the solution was shaken with 0.1 *M* H_2SO_4 (5 ml) then washed several times with water and evaporated. The product was isolated in the usual manner by extraction with ether.

The dihydrochloride was employed for XIIIa. The substance which separated 1—2 days after the addition of the ether was extracted 20 times with ether to leave the product as the residue.

A2. Reaction of $NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2$ *with amine* ($pK_a > 8$) *hydrochlorides in THF at room temperature*

The reaction was carried out and the crude product isolated as in A1. The crude product obtained by filtration of the ethereal suspension was extracted twice with the filtrate and the residue was extracted with CH_3CN (3 × 3—4 ml). The extract was evaporated in a N_2 stream whereupon the product usually crystallized out. When an oil was obtained crystallization was initiated by scratching. The solid was treated with ether (10 ml), then filtered off, and dried in N_2 stream.

In the case of XV the product was extracted with ether (20 ml) 20—25 times in order to remove the oily by-products.

A3. Reaction of $NaBH(NC_4H_4)_2CN \cdot 3C_4H_8O_2$ *with amine* ($pK_a \approx 7$) *hydrochlorides in* CH_3CN *at room temperature*

The reaction and the isolation process was identical with that under A1 but using CH_3CN instead of THF. No ethereal extraction was carried out with XXIV while in the case of XXV the product was the residue after extraction with ether (20 ml) 25—30 times.

B. Thermal decomposition of the ammonium cyanohydrodipyrrolylborates in THF

A solution of the title substance (2.30 mmol) in THF was refluxed for 0.5 h, then filtered, and the filtrate was evaporated under reduced pressure. Ether (15 ml) was added to the oily or semicrystalline residue, and the mixture was agitated a few times during 2—3 h, then filtered. The solid was washed with ether. Additional amounts can be obtained by repeating the evaporation and subsequent processes. After pooling of the two fractions the product was isolated by extraction with ether.

The reaction can also be performed without isolation of the ammonium cyanohydrodipyrrolylborates obtained as under A2, the THF solution being used directly as in B.

In the case of XXVIa the oil obtained after evaporation of the reaction mixture was dissolved in $CHCl_3$ (8 ml) and the solution was extracted with 0.1 *M* HCl (4 × 5 ml), washed with water, dried over a molecular sieve and evaporated under reduced pressure. The residue was kept at 0.01 mbar pressure for 0.5 h.

In the case of XXIXb the THF solution was refluxed for 2 h. The solid obtained upon evaporation was extracted 10—15 times with ether (20 ml). The residue is the product.

In the case of XXXb the product obtained after extraction (6 times) with ether (20 ml) is contaminated with 10% of XXXa.

C1. Base displacement reaction of 4-cyanopyridine-cyanopyrrolylborane (X) with amines

To a suspension of X (0.624 g, 3.00 mmol) in ether (10 ml) is added a stoichiometric amount of base. X goes into solution in a few minutes and the yellow color disappears. The product separates as crystals during this process or after stirring for 0.5 h in the cases of I, XIIa, XXXa and XXXI. It is filtered off, washed with ether, and dried in a N_2 stream.

An oil was obtained in the case of XXIXa, but crystallized upon refluxing the reaction mixture for 1.5—2 h.

In the case of XXXII the reaction mixture was evaporated; the residual oil crystallized spontaneously after a few hours.

In the case of XXXIII, crystallization took place during evaporation. Petroleum ether (20 ml, b.p. 40—60°C) was added, and the solid was filtered off, washed with petroleum ether, and dried in a N_2 stream.

In the case of XXVIa and XXXIV the reaction mixture was evaporated and the 4-cyanopyridine was removed by keeping the residue for 2.5 h at 70°C under reduced pressure (0.01 mbar), the success of this treatment being checked by ^1H NMR. When necessary the oil was dissolved in $CHCl_3$ (5 ml) and the process repeated. The oil was then dissolved in $CHCl_3$ (5 ml) and the solution was washed with 0.1 *M* HCl (5 ml) then with water, dried over A4 molecular sieve, evaporated, and kept under reduced pressure (0.01 mbar) for 0.5—1 h.

C2. Base displacement reaction of 4-cyanopyridine-cyanopyrrolylborane (X) with 4,4'-dipyridyl

X (0.624 g, 3.00 mmol) is extracted from a glass filter into a stoichiometric (2/1, 1/1 or 1/2 molar ratio) amount of 4,4'-dipyridyl (0.234 g, 0.469 g or 0.937 g) in ether (15 ml). The suspension is refluxed for 0.5 h (2 h for XIIIa) then filtered, and the residue washed 3 times with the filtrate then dried.

D. Reaction of 4-cyanopyridine-cyanopyrrolylborane (X) with (—)-(S)- and (+)-(R)-α-phenylethylamine

To an ethereal (20 ml) suspension of X (2.45 g, 11.78 mmol) is added the appropriate title amine (1.46 g, 1.55 ml, 12.05 mmol). After 25 min the solution is evaporated in a N_2 stream and the residual oil is kept under reduced pressure (0.01 mbar) at 65°C for 1.5 h. The residue is dissolved in $CHCl_3$ (6—7 ml), the solution is evaporated under N_2, and the residue is kept under reduced pressure (0.01 mbar) for 1 h, and the whole process is repeated.

The residue is dissolved in a $CHCl_3$ (15 ml) CH_3CN (4 ml) mixture. This solution is washed with 0.1 *M* HCl (first with 4 ml then with 2 ml portions) until the pH of the aqueous layer is <3. It is then washed with water and then dried over Na_2SO_4 and then over A4 molecular sieve. If crystallization occurs during the extraction or drying, the solid is redissolved in a small amount of CH_3CN. The solution is evaporated in a stream of N_2. The crystalline residue is washed on to the filter with ether (20 ml), washed with ether (2 × 2—3 ml), then purified by extraction with pure ether (25—30 ml).

In another procedure the oil (or the mixture of oil and crystals) which remained after three treatments under reduced pressure was repeatedly extracted with $CHCl_3$ (only the oil is dissolved) and the solution evaporated under reduced pressure until (5—7 times) all of the oil is transformed into crystalline material. Thereafter the procedure was as described above.

E. Potassium cyanohydroimidazolylpyrrolylborate-1.5 dioxane (XXXV) and potassium cyanohydropyrazolylpyrrolylborate-1 dioxane (XXXVI)

To a suspension in THF (10 ml) of potassium hydride (0.35 g, 8.73 mmol), a solution of XIIa or VIII (0.74 g, 4.30 mmol) in THF (10 ml) is added with rapid stirring during 10—15 min. The mixture is stirred for another 10 min, then filtered and the filtrate evaporated under reduced pressure to leave a thick syrup.

In the case of XXXV the oil was dissolved in dioxane (15 ml) at 70°C. Two layers separate from the solution, the product crystallizing out from the lower phase during cooling. It is filtered off, washed with dioxane (2 × 2 ml) and dried in a N_2 stream to constant weight.

In the case of XXXVI the oil is dissolved in dioxane (5 ml), and the solution evaporated under reduced pressure. The residue is again dissolved in dioxane (5 ml) and stirred until the product crystallizes out. It is filtered off, washed with dioxane (2 × 2 ml), and dried in a N_2 stream to constant weight.

F. Sodium dicyanohydropyrrolylborate-2 dioxane (XXXVII)

A finely ground mixture of X (0.36 g, 1.73 mmol) and of NaCN (0.17 g, 3.47 mmol) is kept in a bath at 110—115°C under vacuum (0.1—0.01 mbar). After 20 min dioxane (10 ml) is added, the melt is disintegrated mechanicaliy, and the suspension is refluxed for 10 min then filtered. The precipitate is washed with ether and extracted with acetonitrile (10 ml). The extract is evaporated, then the residue dissolved in ether (15 ml) and dioxane (1 ml) is added. The crystalline material is filtered off and purified by washing with the filtrate.

Acknowledgement

We are indebted to Zs. Nagy for valuable assistance in the experimental work, to Dr. L. Szilágyi for recording the NMR spectra and for valuable aid in their interpretation and to Dr. Z. Dinya for the IR spectra and assistance in their interpretation.

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