Pergamon

Polyhedron Vol. 15, No. 21, pp. 3777–3785, 1996

0277-5387/96 $15.00+0.00

S0277-5387(96)00109-X

SYNTHESES OF (N → B)PHENYL[N-ALKYLAMINODIACETATE-O,O′,N]BORANES

TERESA MANCILLA,* LOURDES CARRILLO and MA. DE LA PAZ REDUCINDO

Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Department of Chemistry, Apartado Postal 14-740, 07000, Mexico, D.F.

(*Received* 6 *February* 1996; *accepted* 12 *February* 1996)

Abstract—The syntheses of (N → B)phenyl[N-alkylaminodiacetate-O,O′,N]boranes (**2** to **6**) and their corresponding N-alkylaminodiacetic acids (**7** to **10**) are reported. All compounds (except **6**) were characterized by ^{1}H, ^{11}B (for boron heterocycles), ^{13}C NMR, infrared spectroscopy and mass spectrometry. The ^{1}H NMR spectrum of compound **3** shows that it is a chiral molecule, its structure was determined by homonuclear decoupling experiments, ^{1}H NMR and HETCOR. The study of the intramolecular N → B coordination by dynamic NMR afforded a $\Delta G^{\ddagger}$ value of 98.4 kJ mol^{-1} for compound **3**. Copyright © 1996 Elsevier Science Ltd

We have been interested in the synthesis of bicyclic boron compounds derived from diethanolamines, iminodiacetic acids, and N-alkyl-N-(2-hydroxyethyl)glycines, as well as studying the intramolecular N → B coordination.[1–6] The chemistry of the boron aminoacid derivatives has been little studied in spite of the high degree of hydrolytic stability and the fact that these derivatives are potentially useful for biological studies.[7–12]

There is considerable interest in cyclic boron compounds that present cytotoxic activity,[7,11,15] mainly phenyl derivatives due to the fact that they have also found application in a technique known as boron neutron therapy used for the treatment of certain brain tumors.[16,17]

We have studied the reactivity of boron heterocycles derived from N-methylaminodiacetic and iminodiacetic acid with bases and alkylhalides.[5]

We found that the boron heterocycles of N-methylaminodiacetic acid gave a mixture of α-alkylated compounds.

No apparent reaction occurred on attempted alkylation of **1**, reported previously,[5] because this compound decomposed readily to give phenylboronic acid and iminodiacetic acid.

However, when lithium 2,6-dimethylpiperidide was used as the base, in the presence of the tetramethyl ethylenediamine, the N-substituted boron heterocycles were obtained in low yield.

Recently, we reported the syntheses of new (N → B) phenyl[N-arylaminodiacetate-O,O′,N]boranes and the corresponding N-aryliminodiacetic acid, in this study the bulky lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was chosen as base in order to improve the yield and tetramethylendiamine was not used as in a previous study because it caused problems in the purification of the compounds.[6] This proved to be a new method for the synthesis of N-substituted boron heterocycles, which, in turn, can be hydrolyzed to give the corresponding N-substituted aminodiacetic acids. The latter are more expensive than iminodiacetic acid and only a few are commercially available. Moreover, several N-alkylamino acids have been found to be biologically active.

Consequently, a number of synthetic routes to N-alkylamino acids have been developed,[18] but not for syntheses of N-substituted aminodiacetic acids.

Our current interest in the use of boron heterocycles for the syntheses of new N-substituted aminodiacetic acids prompted us to extend these investigations to prepare N-alkyl derivatives where the alkyl group has another functional group.

This article describes the syntheses of (N → B)phenyl[N - alkylaminodiacetate - O,O′,N]boranes

* Author to whom correspondence should be addressed.

2 to **6** (Fig. 1) and the corresponding N-alkyl-aminodiacetate acids **7** to **10** (Fig. 2).

All compounds were characterized by ^{1}H, ^{11}B (only for compounds **2** to **5**) ^{13}C NMR, infrared spectroscopy and mass spectrometry.

The ^{1}H NMR spectrum of compound **3** showed a complex pattern and its structure was determined by comparison with the chemical shifts of the alkyl halide, homonuclear decoupling experiments and HETCOR.

Moreover application of the coalescence temperature[19] was used to calculate the $\Delta G^{\ddagger}_{coal}$ for compound **3**. Compound **6** was only obtained in low yield when tert-BuLi was used as base. This was only characterized by ^{1}H NMR. Although compound **2** has already been described in the literature,[2,5] we wanted to prove the method used in this work for its synthesis. Compound **7** is commercially available.

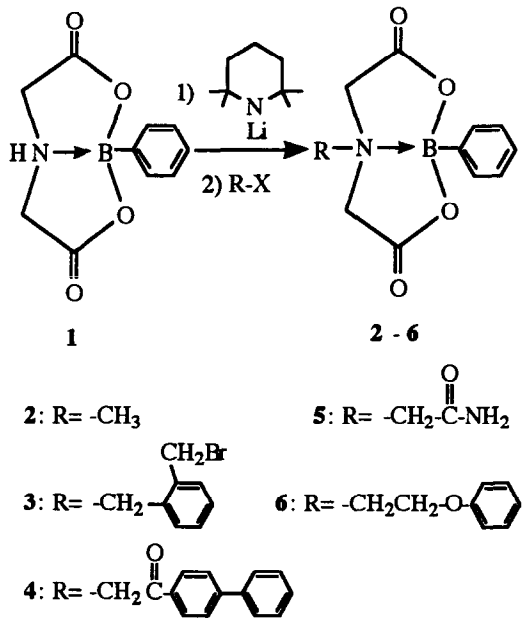


Fig. 1. Synthesis of boron heterocycles **2–5**.

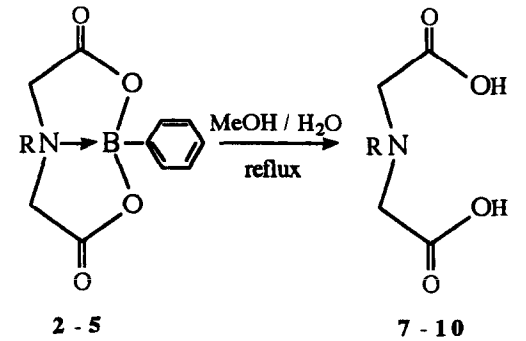


Fig. 2. Synthesis of aminodiacetic acids N-substituted.

EXPERIMENTAL

Chemicals

Reagents were purchased from Aldrich Co. The bicyclic organylboronate **1** was prepared as described previously.[2]

Solvents were dried by standard methods and distilled prior to use.

Preparation of the compounds

The procedure outlined in the following paragraph is general for the preparation of compounds **2** to **5**.

Synthesis of (N → B)*phenyl*[N-*methyl-aminodiacetate*-O,-O′,N]*borane* **2**

A solution of 1.4 cm^3 (2.28 mmol) of n-butyllithium (1.6 M) in hexane was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (TMP) (0.38 cm^3, 2.28 mmol) in THF (10 cm^3) at 0°C. The solution was stirred 30 min at 0°C and 30 min at room temperature and then cooled with a dry ice acetone bath to −80°C. In another flask, a solution of 0.5 g (2.28 mmol) of (N → B)-phenyl [iminodiacetate-O,O′,N]borane **1** in THF (50 cm^3) was cooled to −80°C, and the first solution was transferred to this dropwise.

The reaction mixture was stirred 1 h at −80°C followed by addition of 0.14 cm^3 (2.28 mmol) of methyl iodide. The reaction mixture was stirred 1 h at −80°C. After being warmed to room temperature, the solvent was evaporated *in vacuo*. The yellow solid was treated with 30 cm^3 of acetone, the solution was filtered and the solvent was evaporated *in vacuo*. The remaining white solid was recrystallized from dichloromethane/hexane to yield 0.11 g (20%) of compound **2**, mp 187°C.

Preparation of (N → B)*phenyl*[N(2*methylene-bromide*)*benzylaminodiacetate*-O,O′,N]*borane* **3**

The reaction of 0.5 g (2.28 mmol) of compound **1**, 1.4 cm^3 of n-BuLi, 0.38 cm^3 of TMP and 0.6 g α,α′-dibromo-o-xylene gave 0.20 g (22%) of compound **3** mp 131–132°C.

Synthesis of (N → B)*phenyl*[N(4-*phenyl*)*phenacyl-amino-diacetate*-O,O′,N]*borane* **4**

The reaction of 0.5 g (2.28 mmol) of compound **1**, 1.4 cm^3 of n-BuLi, 0.38 cm^3 of TMP and 0.6 g (2.28 mmol) of 4-phenylphenacyl bromide gave 0.37 g (39%) of compound **4**, mp 197–198°C.

Synthesis of (N → B)*phenyl*[N-*carbamoylmethyl-aminodiacetate*-O,O′,N]*borane* **5**

The reaction of 0.5 g (2.28 mmol) of compound **1**, 1.4 cm^3 of n-BuLi, 0.38 cm^3 of TMP and 0.4 g (2.28 mmol) of iodoacetamide gave 0.21 g (43%) of compound **5**, mp 185–187°C.

Synthesis of (N → B)*phenyl*[N(*ethylphenyl-ether*) *aminodiacetate*-O,O′, N]*borane* **6**

A solution of 2.28 mmol (1.3 cm^3) of tert-butyllithium (1.7 M) in pentane was added dropwise to a stirred solution of 0.5 g (2.28 mmol) of compound **1** in 40 cm^3 of THF at −80°C. The solution was stirred 2 h at −80°C followed by addition of a solution 0.45 g of 2-bromo(ethyl phenyl ether) in 5 cm^3 of THF. The reaction mixture was stirred 24 h at room temperature. After, the solvent was evaporated *in vacuo*, the remaining solid was treated with acetone. The ^1H NMR spectrum shows the signals corresponding to the compound **1** as major product and the signals for compound **6** as minor product.

The procedure outlined in the following paragraph is general for the synthesis of compounds **7** to **10**.

Synthesis of N-methylaminodiacetic acid **7**

A mixture of methanol/water (50 : 50) was added to 0.1 g (0.42 mmol) of (N → B)phenyl[N-methyl-aminodiacetate-O,O′,N]borane **2**. The reaction mixture was refluxed during 2 h. The solvent was eliminated by vacuum distillation, and the solid obtained was recrystallized from acetone to yield 0.024 g of compound **7** (38%), mp 210°C (decomp).

Synthesis of N-(2-methylenebromide)benzylamino-diacetic acid **8**

A 0.1 g (0.24 mmol) amount of compound **3** gave 0.02 g of compound **8** (25%) mp 159°C.

Synthesis of N-(4-phenyl)phenacylaminodiacetic acid **9**

A 0.1 g (0.24 mmol) amount of compound **4** gave 0.06 g of compound **9** (79%) mp 196–198°C.

Synthesis of N-carbamoyl methyl aminodiacetic acid **10**

A 0.1 g (0.38 mmol) amount of compound **5** gave 0.02 g of compound **10** (31%) mp 200°C (decomp).

Instrumentation

All ^1H and ^{13}C chemical shifts are reported relative to TMS and ^{11}B relative to $BF_3OC_2H_5$, using DMSO-d_6 as solvent. Mass spectra were obtained with a Hewlett Packard 59940-A instrument, and infrared spectra were determined on a Perkin-Elmer 16F PC FT-IR spectrometer.

Melting points were taken in open capillary tubes on a Gallenkamp MFB-595 apparatus and are uncorrected.

RESULTS AND DISCUSSION

Synthesis

The reaction of (N → B)phenyl[iminodiacetate-O,O′,N]borane **1** with lithium 2,2,6,6-tetramethylpiperidide and alkyl halides led to (N → B)phenyl[N-alkylaminodiacetate-O,O′,N]boranes (**2** to **5**) (Fig. 1). Compound **6** could be obtained in low yield when tert-butyllithium was used as base. These compounds were obtained as air-stable solids by recrystallization from methylene chloride/hexane.

^1H NMR data of the compounds **2**–**6** are summarized in Table 1. The spectra clearly show the AB coupling pattern for the diastereotopic CH_2-COO protons, which indicates the presence of the intramolecular N → B coordination bond.

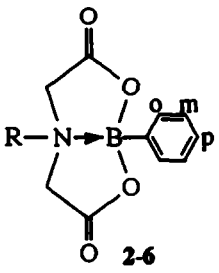
The ^1H NMR spectrum of compound **3** showed two AB coupling patterns for two diastereotopic CH_2-COO protons, this can be explained on the basis of restricted rotation of the N—R bond due to the presence of the *o*-CH_2-Br group in R. In fact, the R group showed an ABX_2 system for the methylene groups. Its assignment was achieved by homonuclear proton decoupling experiment ^1H $\{^1H\}$, decoupling the triplet signal at δ 4.85, this reduced the doublet of doublets signal at δ 3.35 and 3.20 to an AB spin system. The triplet signal was assigned to the two disastereotopic N-$C\underline{H}_2$(*o*-$CH_2BrC_6H_4$) protons and the doublet of doublets signal to the two diasterotopic N-CH_2(*o*-$C\underline{H}_2BrC_6H_4$) protons.

The spectra of compounds **2** to **6** showed an unresolved pattern at δ 7.5 and 7.3 assigned to $H_{(o)}$ and $H_{(m,p)}$, respectively, for the B-phenyl group.

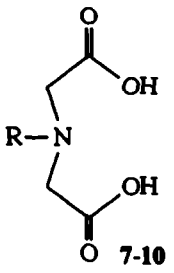
The H_m, H_p protons of the R group in compounds **3** and **6** are overlapped with those corresponding to the B-phenyl group.

Furthermore, a variable temperature experiment in the ^1H NMR of compound **3** shows coalescence of the AB system, at δ 3.81 and 3.78 for the $C\underline{H}_2COO$ protons at 180°C. This is interpreted by a dissociation–inversion mechanism observed for

Table 1. ^1H and ^{11}B NMR data for compounds **2** to **10**

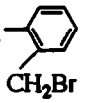


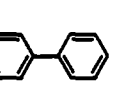
2-6



7-10

2,7 R= -CH_3

3,8 R= -CH_2- 

4,9 R= -CH_2-C(=O)- 

5,10 R= -CH_2-C(=O)-NH_2

6 R= -CH_2-CH_2-O- 

Compound	CH_2-COO	N-CH_3	N-CH_2	N-R CH_2Br	$H_{aromatic}$	B-Ph	$\delta^{11}B$
2	H_A: 4.35 (d) H_B: 4.10 (d) J = 17.15	2.49 (s)				H_o: 7.44 (m) $H_{m,p}$: 7.39 (m)	+11.21
3	H_A: 3.81 (d) H_B: 3.78 (d) J = 13.86 H_A: 4.52 (d) H_B: 3.90 (d) J = 17.16		4.85 (t) J = 5.9	H_A: 3.35 (dd) H_B: 3.20 (dd) J = 590 J = 15.50	6.64 (d) J = 7.27 7.1–7.5 (m)	7.1–7.50 (m)	+11.87
4	H_A: 4.60 (d) H_B: 4.35 (d) J = 17.15		4.59 (s)		7.81 (d) J = 8.6 7.72 (d) J = 6.6 7.62 (d) J = 8.0	H_o: 7.49 (m) $H_{m,p}$: 7.41 (m)	+11.00
5[a]	H_A: 4.43 (d) H_B: 4.28 (d) J = 17.15		3.38 (s) 8.04 (b)			H_o: 7.37 (m) $H_{m,p}$: 7.43 (m)	+12.00
6[b]	H_A: 4.50 (d) H_B: 4.25 (d) J = 17.15		3.03 (t) 3.96 (t) J = 6.3		H_o: 7.78 (dd) J = 7.9 J = 1.98	7.3–7.5 (m)	
7	3.40 (s)	2.44(s)					
8	H_A: 3.63 (d) H_B: 3.52 (d) J = 17.82		H_A: 3.90 (d) H_B: 3.81 (d) J = 3.93	H_A: 3.10 (d) J = 5.3 H_B: 3.00 (d) J = 3.3	7.04 (m) 7.11 (b) 7.12 (b)		
9	3.56 (s)		4.34 (s)		8.08 (d) 7.81 (d) J = 8.6 7.75 (d) 7.51 (d) 7.45 (d) J = 7.15		
10	3.57 (s)		4.80 (s)				

δ (^1H) relative to Si $(CH_3)_4$; δ (^{11}B) relative to $BF_3OC_2H_5$; solvent DMSO-d_6.

[a] The broad signal at 8.04 ppm is assigned to the $N\underline{H}_2$ protons.

[b] Compound **6** was only characterized by ^1H NMR, the signals of $H_{m,p}$ of the R group are overlapped with those of the B-Ph group.

b: broad; d: doublet; dd: doublet of doublets; m: unresolved pattern; s: singlet; t: triplet and |J| Hz.

bicyclic boron compounds derived from diethanolamines,[1,13] but not found in iminodiacetic acids derivatives of similar structure,[2] which have been shown to be highly stable to hydrolysis with an extremely stable N → B bond.[2,6]

Application of the coalescence temperature was

used to calculate the $\Delta G^{\ddagger}_{coal}$ for compound **3**. The $\Delta G^{\ddagger}_{coal}$ 98.4 kJ/mol for compound **3** reveals its increased stability in comparison with the corresponding $\Delta G^{\ddagger}_{coal}$ obtained for the boron heterocycle derivate of N-methyldiethanolamine (73.1 kJ/mol).[13]

The $\delta(^{11}B)$ values (Table 1) confirm the tetrahedral environment of the ^{11}B nucleus, since they lie in the range reported previously for analogous boron heterocycles.[1,6]

Table 2 shows that compounds **2** to **5** exhibit the expected ^{13}C NMR spectra.

The assignments for C_1, C_2, C_o, C_m, and C_p for compounds **2** to **5** were achieved by comparison with the chemical shifts of bicyclic boron compounds reported by us previously.[2,5,6] In the case of compound **3** the spectrum shows two signals for two diastereotopic C_1 and C_2.

The assignment for C_3 (N-R group): in compound **2** was deduced by comparison with the chemical shift reported by us previously.[5]

The assignment for C_3 in **3** was obtained using the ^{13}C-^1H HETCOR spectrum correlating the proton signal to the carbon signal, this shows the correlation between the proton signals of N-C<u>H</u>$_2$C$_6$H$_4$ (*o*-CH$_2$Br) from the R group and the signal due to C_3 at δ 66.4, therefore, the protons of *o*-C<u>H</u>$_2$Br group show an AB pattern, which is correlated with the carbon signal at δ 27.8 assigned to C_8.

The assignments for carbons of the aromatic rings from the R group for compounds **3** and **4** were achieved by comparison with the chemical shifts of bicyclic boron compounds reported by us previously.[5,6]

Characteristic IR bands of the investigated compounds are summarized in Table 3.

Compounds **2** to **5** show two bands due to the carbonyl functions of the ester located between 1764–1732 cm^{-1} and 1739–1638 cm^{-1}, a band due to the presence of the B—O group in the range of 1396–1300 cm^{-1} and the band due to the presence of the N → B group at 1025–1040 cm^{-1}.

The 70 eV EI mass spectra of compounds **2**, **4** and **5** exhibit the molecular ion. Compound **3** does not exhibit the molecular ion, however it shows the fragment ions at m/z = 322 (11%) and 321 (45%), corresponding to the loss of the Br and BrH groups, respectively.

The following important fragment ions are observed, spectra of **2**, **4** and **5** exhibit fragment ions at m/z = 156, 336 and 199, respectively with relative abundance of 8%, 22% and 1%, respectively, corresponding to the loss of the B—<u>Ph</u> group from the molecular ion. Spectra of **2** and **3** exhibit a fragment ion at m/z = 128 (48%) and 216 (14%), respectively, which correspond to the loss of —CO group from the fragment ions at m/z = 156 and 336, respectively.

Compound **2** shows the fragment ion at m/z = 176 (100%), which corresponds to the loss of the CHCOO group from molecular ion. The spectra show the corresponding base peak at m/z = 132 for compound **3**, m/z = 28 for compound **4** and m/z = 42 for compound **5**. The fragmentation pattern proposed is given in Fig. 3.

Moreover the mass spectra of compounds **2** to **5** exhibit other fragment ions that are characteristic for each compound. The following fragment ions are also observed for compound **2**: m/z = 57 $[CHCO_2]^+$, m/z = 100 $[CH_3(CH_2)NCH_2OBO]^+$ and m/z = 42 $[CH_2{=}N{=}CH_2]^+$, with relative abundance of 50%, 70% and 89%, respectively.

The spectrum of **3** exhibits the fragment ions at m/z = 320 (15%), 293 (13%), corresponding to the loss of —H and —CO group, respectively, from the fragment ion of m/z = 321.

These last fragment ions lose the phenyl group bonded at the boron to give the fragment ions at m/z = 243 (22%) and 216 (14%), respectively, which can lose CO and H to give the fragment ion at m/z = 215 (12%). The fragmentation pattern proposed is given in Fig. 4.

Figure 5 shows other important fragment ions observed for **3**.

The mass spectrum of compound **4** shows the following fragment ions: at m/z = 196 (30%) $[C_6H_5C_6H_4COCH_3]^+$, m/z = 151 (79%) $[C_6H_5C_6H_4CO]^+$ and m/z = 153 (26%) $[C_6H_5C_6H_4]^+$.

The spectrum of compound **5** shows also the fragment ions proposed in Fig. 6.

Hydrolysis of compounds **2** to **5** gave the aminodiaceticacids N-substituted **7** to **10** respectively (Fig. 2). Table 1 shows the ^1H NMR spectra of compounds **7** to **10**, which exhibit the expected resonances.

These compounds show a single signal for C<u>H</u>$_2$-COOH protons, except **8**, which shows an AB coupling pattern due to the chirality of the molecule. It shows two AB systems for both methylene protons from R group.

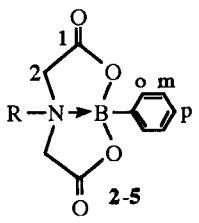
Table 2 shows the expected ^{13}C NMR spectra for compounds **7** to **10**. The assignments for C_1 to C_{12} were achieved in the same way as for compounds **2** to **5**.

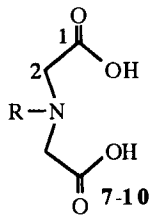
Table 3 shows infrared data for compounds **7** to **10**. The infrared absorption of the carbonyl functions are indicative of the presence of carboxylic acid groups.

The 70 eV EI mass spectra of compounds **7**–**10** did not exhibit the molecular ion.

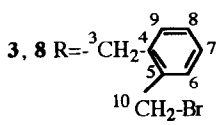
The following important fragment ions were observed.

Table 2. ^{13}C NMR data for compounds **2** to **5** and **7** to **10**





2, **7** R=-$^{3}CH_3$



Compound	R												B-Ph		
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_o	C_m	C_p
2	168.3	61.7	47.5										132.3	127.6	128.8
3	168.3	54.9	66.4	137.5	134.0	130.3	127.3	126.7	128.9	27.8			132.5	127.4	128.8
	171.3	61.1													
4	169.7	60.7	64.9	192.0	145.2	128.1	126.8	133.9	132.9	129.0	126.9	127.2	132.5	127.6	128.6
5	169.6	57.7	60.4	173.3									132.5	127.5	128.8
7	171.1	56.7	41.5												
8	171.8	50.2	58.4	133.9	133.2	128.3	125.8	125.6	126.0	31.3					
	173.5	56.0													
9	172.4	55.0	60.0	197.2	144.5	128.6	126.7	138.8	134.3	128.9	126.8	128.3			
10	174.4	61.3	70.8	165.1											

δ: (ppm); solvent DMSO-d_6.

Table 3. IR data for compounds **2–5** and **7–10**

Compound	C—H_{arom}	C—H_{aliph}	C=O	B—O	N → B
2	3114	2962	1764	1300	1025
			1739		
3	3076	2932	1758	1312	1026
		2860	1640		
4	3096	2938	1732	1396	1034
		2864	1638		
5	3082	2934	1738	1368	1040
		2862	1642		
7		2950	1740		
			1683		
8	3050	2934	1732		
		2862	1640		
9	3090	2937	1734		
			1682		
			1642		
			1604		
10		2934	1644		
		2864			

ν (cm^{-1}), KBr.

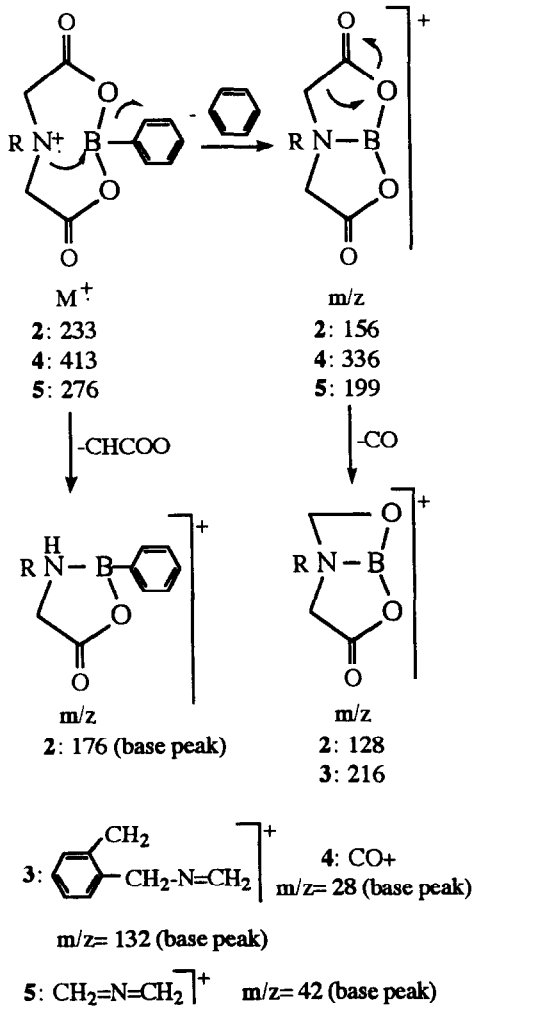


Fig. 3. Mass spectral data of boron heterocycles **2–5**.

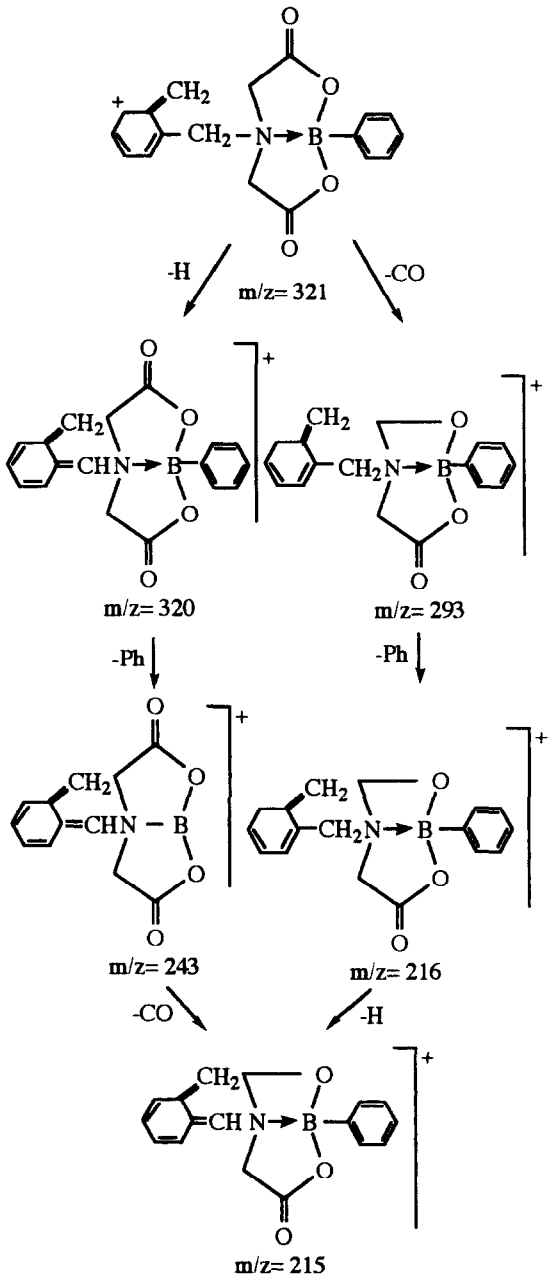


Fig. 4. Mass spectral data of compound **3**.

Spectrum of **7** exhibits a fragment ion at $m/z = 69$ (22%) $[CH_2{=}N{-}CH{=}C{=}O]^+$, $m/z = 43$ (18%) $(CH_3{-}N{=}CH_2]^+$, $m/z = 29$ (13%) $[CH_2{-}NH]^+$ and the base peak at $m/z = 18$ $[H_2O]^+$.

The spectrum of **8** exhibits an ion fragment at $m/z = 236$ with relative abundance of 2%, corresponding to the loss of Br ion from the molecular ion, the fragment ions at $m/z = 191$ (14%) and 177 (4%), corresponding to the loss of CO_2H and CH_2COOH group, respectively from the fragment ion at $m/z = 236$. The fragment ion at $m/z = 190$ which corresponds to the base peak and the frag-

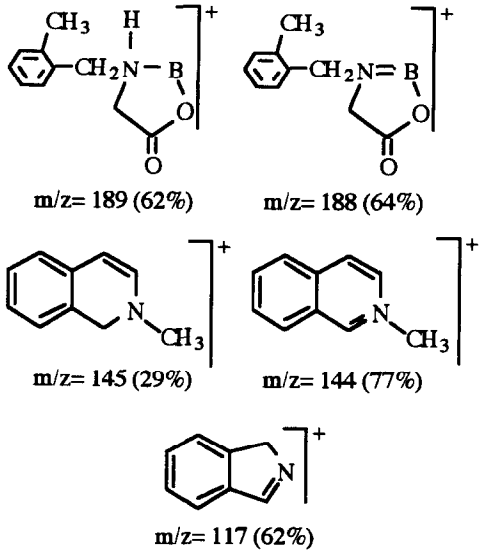


Fig. 5. Fragment ions observed for compound **3**.

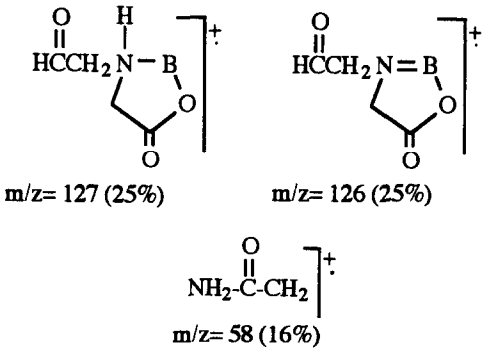


Fig. 6. Fragment ions observed for compound **5**.

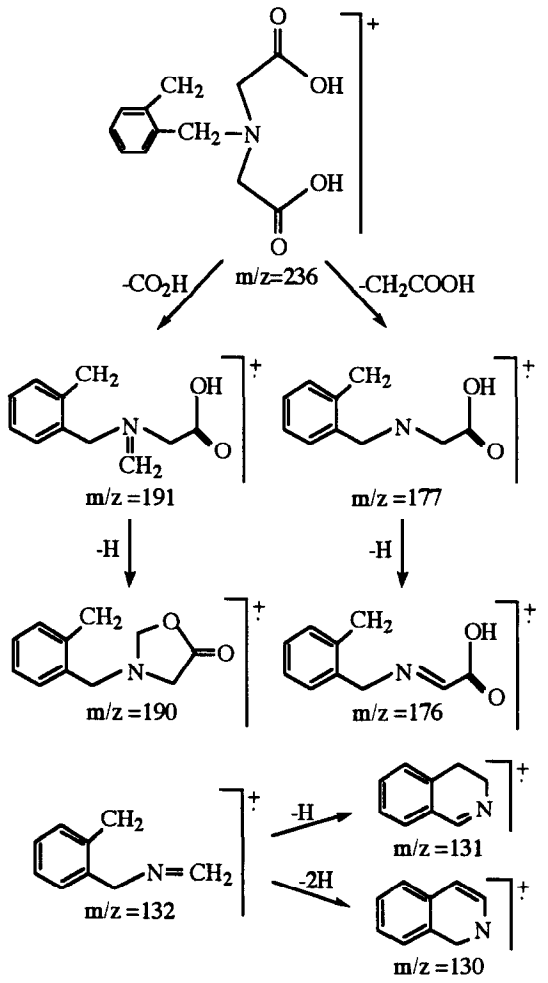


Fig. 7. Mass spectral data of compound **8**.

ment ion at $m/z = 176$ (29%) corresponding to the loss of H ion from fragments ions at $m/z = 191$ and 177. The fragment ion at $m/z = 132$ (18%), corresponds to the loss of the COOH group from the fragment ion at $m/z = 177$. The fragment ion at $m/z = 132$ can lose a H and 2H to give the fragment ions at $m/z = 131$ (33%) and 130 (36%), respectively. The fragmentation pattern proposed is given in Fig. 7.

The spectrum of compound **9** exhibits the following fragment ions: $m/z = 196$ (3%) $[C_6H_5C_6H_4COCH_3]^+$, $m/z = 181$ (7%) $[C_6H_5C_6H_4CO]^+$, $m/z = 153$ (3%) $[C_6H_5C_6H_4]^+$, $m/z = 57$ (7%) $[NH{=}CH_2CO]^+$, $m/z = 55$ (8%) $[N{=}CH{=}CO]^+$, m/z 45 (45%) $[COOH]^+$, $m/z = 44$ (100%) $[CO_2]^+$, $m/z = 43$ (16%) $[CH_3N{=}CH_2]^+$, $m/z = 42$ (12%) $[CH_2{=}N{=}CH_2]^+$, $m/z = 28$ (16%) $[CO]^+$, $m/z = 18$ (17%) $[H_2O]^+$ and compound **10** exhibits the following important fragment ions: $m/z = 142$ (15%), $m/z = 141$ (18%), $m/z = 127$ (56%), $m/z = 58$ (100%) (see Fig. 8), $m/z = 45$ (20%) $[COOH]^+$, $m/z = 44$ (40%) $[CO_2]^+$ and $m/z = 28$ (36%) $[CO]^+$.

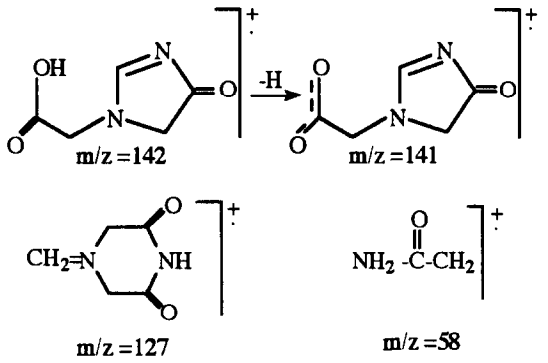


Fig. 8. Mass spectral data for compound **10**.

Acknowledgements—The authors would like to thank "Consejo Nacional de Ciencia y Tecnología" (CONACYT) for financial support, and Dr Rosa Luisa Santillán B. for reading the manuscript and for her helpful comments.

REFERENCES

1. R. Contreras, C. Garcia, T. Mancilla and B. Wrackmeyer, *J. Organomet. Chem.* 1983, **246**, 213.
2. T. Mancilla, R. Contreras and B. Wrackmeyer, *J. Organomet. Chem.* 1986, **307**, 1.
3. T. Mancilla and R. Contreras, *J. Organomet. Chem.* 1987, **321**, 191.
4. N. Farfán, T. Mancilla, D. Castillo, G. Uribe, L. Carrillo, P. Joseph-Nathan and R. Contreras, *J. Organomet. Chem.* 1990, **381**, 1.
5. T. Mancilla and S. L. Galvez, *Main Group Met. Chem.* 1992, **15**, 9.
6. T. Mancilla, Ma. L. Alarcón and L. Carrillo, *Heteroatom Chem.* 1994, **5**, 455.
7. G. Baum, *J. Organomet. Chem.* 1970, **22**, 269.
8. K. Lang, K. Nützel and F. Schubert, Ger. pat., 1130445, 1962, *Chem. Abstr.* 1963, **58**, 448.
9. K. Becker, in *Gmelin Handbuch der Anarganischen Chemie*, 1346, T15. Springer Verlag, Berlin, Heidelburg, New York (1977).
10. S. H. Tung, K. M. Chang, S. L. Tah, C. L. Liu and S. L. Chang, *K'o Hsueh T'ung Pao.* 1966, **17**, 414. *Chem. Abstr.* 1967, **66**, 37990 m.
11. B. Garrigues, M. Mullier and A. Raharinirina, *J. Organomet. Chem.* 1986, **302**, 153.
12. N. E. Miller, *Inorg. Chem.* 1974, **13**, 1459.
13. R. Csuk, H. Hönig and C. Romanin, *Monatsh. Chem.* 1982, **113**, 1025.
14. R. Csuk, N. Müller and H. Sterk, *Z. Naturforsch B* 1985, **40**, 987.
15. R. Csuk, H. Hönig, H. Weidmann and H. K. Zimmerman, *Arch. Pharm.* 1984, **317**, 336.
16. C. A. Perks, A. J. Mill, G. Constantine, K. G. Harrison and J. A. B. Gibson, *British J. Radiol.* 1988, 61.
17. H. Nemoto, J. Cai and N. Asao, *J. Med. Chem.* 1995, **38**, 1673.
18. W. Oppolzer, P. Cintas-Moreno, O. Tamura and F. Cardinaux, *Helv. Chim. Acta* 1993, **76**, 187.
19. R. J. Abraham and P. Loflus, in *Proton and Carbon-13 NMR Spectroscopy* p. 167. Hyden (1980).