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Synthesis and characterization of some amine complexes of bromocarboxyboranes and bromo(methoxycarbonyl)boranes

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Abstract

Amine-carboxyboranes [A.BH_2COOH; A = Me_3N, Et_3N, quinuclidine (Q)] are readily decarbonylated with bromine in dichloromethane to produce amine-dibromoboranes (A.$BHBr_2$). The formation of A.$BHBr_2$ is explained by fast loss of CO from the acid bromides A.BH(Br)COBr generated because of the action of HBr. In proton–acceptor solvents (such as H_2O), however, only substitution takes place giving a chiral boron atom containing A.BH(Br)COOH and/or A.BBr_2COOH. Also, bromocarboxyborane complexes can be prepared easily using bromination with *N*-bromosuccinimide (NBS). The products are rather stable in water under acidic conditions but bases induce fast decarbonylation followed by complete decomposition. Amine-(methoxycarbonyl)boranes A.BH_2COOMe (A = Me_3N, Et_3N and Q) are conveniently synthesized, with good yields, in methanol by treatment with a cation exchange resin (H^+) as a catalyst. The bromo derivatives A.$BH_{2-n}Br_nCOOMe$ (n = 1, 2) have been prepared by treatment of amine complexes of BH_2COOMe with bromine or NBS, or by esterification of the bromocarboxylic derivatives. In addition, these bromo compounds can be readily obtained in a one-pot reaction from A.BH_2COOH with bromine; when esterification proceeds unexpectedly fast in parallel with the bromination. The structures of the new derivatives were substantiated by elemental analyses and IR, UV, ^1H NMR and ^{11}B NMR spectroscopic methods.

Keywords: Boron; Carboxyborane; Bromoborane; Bromination; Decarbonylation; Chiral boron atom

1. Introduction

During the past 15 years several amine-carboxyboranes and their derivatives (amine-BH_2X; where X = COOH, COOR, $CONR_2$, CSNHR, C(OR) = NR, C(CN) = NR, CN, etc.) have been synthesized [1–13]. These compounds, considered as the boron analogues of protonated α-amino acids and their derivatives [1,12], possess extensively demonstrated hypolipidemic [14,15], anticancer [16] and antiinflammatory [17] powers. The promising biological activities have generated considerable interest in synthesizing novel types of carboxyboron compounds including derivatives with a P–B bond [15,18]. At the same time, little effort has been devoted to preparing boron-substituted derivatives of amine-BH(Y)X and amine-BY_2X structures [6,8]. The monosubstituted derivatives may be particularly interesting as they have a chiral boron atom.

Since bromine linked to a boron atom has been observed as a good leaving group [19], it might easily be exchanged with other functions such as R, OR, SR, NR_2, CN, etc. Preliminary studies in this laboratory show that a Br^--amine exchange can be easily manipulated to produce hitherto unknown carboxyboron(1 +) ions [2a]. Here we report on the synthesis of mono and dibromo derivatives of several amine-carboxyboranes. As the acidic hydrogen of such compounds may disturb the exchange of bromine into another functional group, the methyl ester derivatives of the amine-bromocarboxyboranes have also been synthesized.

2. Experimental details

2.1. General comments

With the exception of the reactions performed in an aqueous medium the experiments were carried out by using the Schlenk techniques in a nitrogen atmosphere [21]. All the evaporations were made under diminished pressure and the products were dried in a N_2-stream at room temperature. Extractions of the solid materials were carried out according to the standard Schlenk

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periodic extraction technique [21]. The solvents used were also free from water and oxygen. Methanol and ether were distilled from magnesium methoxide (Mg/I_2) and Na-benzophenone, respectively, and purification of dichloromethane was carried out by distillation from CaH_2 and then P_2O_5. Chloroform was first made free from alcohol and then distilled from P_2O_5. $Me_3N.BH_2COOH$ (**1a**) [11, 16], $Et_3N.BH_2COOH$ (**1b**) and $Q.BH_2COOH$ (**1c**) [2b,22] were prepared according to known procedures.

The boron and bromine content of the samples was determined with acid–base titration in the presence of mannitol, or by using the Volhard method, respectively, after fusion with sodium hydroxide and potassium hydroxide. Analysis of the evolved gases (H_2 and CO) was carried out with a QGA-2(ATOMKI) quadrupole mass spectrometer. The UV and IR spectra were recorded with Varian DMS 100S and Perkin-Elmer 16PC FT–IR spectrometers and the NMR spectra were obtained with a Bruker WP 200 SY instrument. Internal TMS and boron trifluoride ethyl ether complex in a coaxial tube were used as references for the ^1H and ^{11}B NMR spectra, respectively. The IR and NMR data are summarized in Table 1.

2.2. Preparation of $A.BH_2COOMe$ [$A = Me_3N$ (2a), Et_3N (2b) and Q (2c)]

To a solution of the amine-carboxyborane (18.0 mmol) in methanol (30 ml) Dowex AG 50 W cation

Table 1
Spectroscopic data for new (methoxycarbonyl)- (**2**), monobromocarboxy- (**3**), dibromocarboxy- (**4**), monobromo(methoxycarbonyl)- (**5**) and dibromo(methoxycarbonyl)borane (**6**) complexes formed with amines (A)

Compound	^1H NMR [a] δ (ppm)	^{11}B NMR [a] δ (ppm), J(B–H) (Hz)	IR [b] ν(B–H) (cm^{-1})	IR [b] ν(C=O) (cm^{-1})
2b	1.15 (t, 9H, NCH_2CH_3) 3.06 (q, 6H, NCH_2CH_3) 3.52 (sg, 3H, OCH_3)	−14.47 (t), 101.7	2402	1666
2c	1.78 (m, 6H, $N(CH_2CH_2)_3CH$) 2.04 (h, 1H, $N(CH_2CH_2)_3CH$) 3.22 (t, 6H, $N(CH_2CH_2)_3CH$) 3.52 (sg, 3H, OCH_3)	−11.1 (t), 97.7	2378 2354	1670
3a	2.92 (sg, 9H, NCH_3)	−5.62 (d), 123.9	2476	1654
3b	1.26 (t, 9H, NCH_2CH_3) 3.32 (q, 6H, NCH_2CH_3)	−6.43 (d), 112.8	2492	1654
3c	1.83 (m, 6H, $N(CH_2CH_2)_3CH$) 2.11 (h, 1H, $N(CH_2CH_2)_3CH$) 3.42 (m, 6H, $N(CH_2CH_2)_3CH$)	−6.23 (d), 109.6	2468	1646
4a	3.17 (sg, 9H, NCH_3)	−2.36 (sg)	–	1662
4b	1.38 (t, 9H, NCH_2CH_3) 3.63 (q, 6H, NCH_2CH_3)	−2.54 (sg)	–	1654
4c	1.88 (m, 6H, $N(CH_2CH_2)_3CH$) 2.18 (h, 1H, $N(CH_2CH_2)_3CH$) 3.73 (m, 6H, $N(CH_2CH_2)_3CH$)	−2.28 (sg)	–	1652
5a	2.91 (sg, 9H, NCH_3) 3.62 (sg, 3H, OCH_3)	−5.41 (d), 124.5	2474	1680
5b	1.25 (t, 9H, NCH_2CH_3) 3.32 (dt, 6H, NCH_2CH_3) 3.61 (sg, 3H, OCH_3)	−6.57 (d), 111.0	2500	1682
5c	1.84 (m, 6H, $N(CH_2CH_2)_3CH$) 2.11 (h, 1H, $N(CH_2CH_2)_3CH$) 3.41 (m, 6H, $N(CH_2CH_2)_3CH$) 3.60 (sg, 3H, OCH_3)	−6.06 (d), 125.5	2474	1686
6a	3.16 (sg, 9H, NCH_3) 3.69 (sg, 3H, OCH_3)	−2.39 (sg)	–	1682
6b	1.36 (t, 9H, NCH_2CH_3) 3.63 (q, 6H, NCH_2CH_3) 3.68 (sg, 3H, OCH_3)	−2.01 (sg)	–	1678
6c	1.88 (m, 6H, $N(CH_2CH_2)_3CH$) 2.18 (h, 1H, $N(CH_2CH_2)_3CH$) 3.67 (sg, 3H, OCH_3) 3.74 (t, 6H, $N(CH_2CH_2)_3CH$)	−2.25 (sg)	–	1678

A = trimethylamine (**a**), triethylamine (**b**) and quinuclidine (**c**).
[a] Solvent: $CDCl_3$.
[b] Recorded in KBr pellets, except **5b**, which was recorded in nujol.

exchange resin (1.1 g; H^+ form; dried over P_2O_5) was added. The reaction mixture of **2a**, **2b** and **2c** was refluxed for 8, 6 and 4 hours, respectively, and then the resin was filtered off and washed with methanol (3 × 5 ml). The filtrate was evaporated to dryness. In the case of **2b** *n*-pentane (10 ml) was added to the syrupy residue and it was evaporated to dryness. **2a**: yield 2.04 g, 86%. Anal. Found: B, 8.14. Calc. for $C_5H_{14}BNO_2$: B, 8.25%. **2b**: yield 2.60 g, 82%. Anal. Found: B, 6.20. Calc. for $C_{18}H_{20}BNO_2$: B, 6.25%. **2c**: yield 2.51 g, 76%. Anal. Found: B, 5.94. Calc. for $C_9H_{18}BNO_2$: B, 5.91%.

2.3. Preparation of amine-bromocarboxyboranes

2.3.1. A.BH(Br)COOH [A = Me_3N (3a), Et_3N (3b), Q (3c)] from 1a–c with NBS in chloroform

To a suspension of *N*-bromosuccinimide (1.03 g; 5.8 mmol) in chloroform (5 ml) a solution of the amine-carboxyborane (5.8 mmol) in chloroform (50 ml) was added (for dissolution gentle heating may be required). After 5 min reaction time the mixture was evaporated to dryness and the residue was taken up with petroleum ether (10 ml; bp. 40–70°C), filtered, washed with cold (0°C) water (4 × 3 ml) and dried. **3a**: yield 0.93 g, 81%. Anal. Found: B, 5.46; Br, 40.70. Calc. for $C_4H_{11}BBrNO_2$: B, 5.52; Br, 40.80%. **3b**: yield 1.07 g, 77%. Anal. Found: B, 4.49; Br, 33.59. Calc. for $C_7H_{17}BBrNO_2$: B, 4.54; Br, 33.58%. **3c**: yield 1.35 g, 94%. Anal. Found: B, 4.33; Br, 32.29. Calc. for $C_8H_{15}BBrNO_2$: B, 4.36; Br, 32.23%.

2.3.2. Me_3N.BH(Br)COOH (3a) from 1a with bromine in water

To a suspension of **1a** (0.412 g; 3.52 mmol) in water (2 ml) bromine water (16.5 ml; 0.214 M) was added dropwise at 0°C. The reaction mixture was stirred at 0°C for 10 min, then filtered and the filtrate was washed with ice-water (3 × 2 ml) and dried. Compound **3a** was separated from the crude product by five times extraction with chloroform (20 ml), the extract was evaporated to a 5 ml volume, the product was filtered, washed with chloroform (2 × 2 ml) and dried. Yield 0.45 g, 66%. Anal. Found: B, 5.56; Br, 40.88%.

2.4. Preparation of A.BBr_2COOH [A = Me_3N (4a), Et_3N (4b) and Q (4c)]

To an aqueous suspension (5 ml) of the amine-carboxyborane (6.0 mmol) bromine water (74.0 ml; 0.180 M) was added with stirring at 0°C and the mixture was stirred at the same temperature for 4 h. After filtration the filtrate was washed with water (3 × 5 ml) and dried. The crude products **4a**, **4b** or **4c** were purified by 20–40 times extraction with ether (30 ml) or dichloromethane (30 ml), respectively. The pure products, precipitated from the extracts, were filtered and washed with ether or dichloromethane (2 × 5 ml), respectively, then dried. **4a**: yield 1.17 g, 71%. Anal. Found: B, 3.88; Br, 57.81. Calc. for $C_4H_{10}BBr_2NO_2$: B, 3.93; Br, 58.17%. **4b**: yield 1.23 g, 65%. Anal. Found: B, 3.40; Br, 50.30. Calc. for $C_7H_{16}BBr_2NO_2$: B, 3.41; Br, 50.44%. **4c**: yield 1.57 g, 80%. Anal. Found: B, 3.26; Br, 48.40. Calc. for $C_8H_{14}BBr_2NO_2$: B, 3.31; Br, 48.90%.

2.5. Preparation of amine-monobromo(methoxycarbonyl)boranes

2.5.1. A.BH(Br)COOMe [A = Me_3N (5a), Et_3N (5b) and Q(5c)] from 2a–c with bromine in methanol

To a solution of the amine-(methoxycarbonyl)borane (4.0 mmol) in methanol (20 ml) a solution of bromine in methanol (16.3 ml, 0.25 M) was added over 5–10 min under vigorous stirring. (For the preparation of **5b** the same manipulation was carried out at −20°C in a half an hour.) The reaction mixture was evaporated immediately (in the case of **5b** the residue is a syrup). When preparing **5a** the residue was dissolved in ether (15 ml), the small amount of the insoluble material was filtered off, the filtrate was evaporated to dryness, the residue was taken up with *n*-pentane (6 ml), filtered and then washed with *n*-pentane (2 × 1 ml) and dried. Yield 0.70 g, 83%. Anal. Found: B, 5.19; Br, 37.84. Calc. for $C_5H_{13}BBrNO_2$: B, 5.15; Br, 38.07%. The crude syrupy **5b** was treated thre to four times with ether (4 ml) and repeatedly evaporated until a non-sticky substance was precipitated. The suspension was diluted with ether (2–3 ml), filtered and the filtrate evaporated. The residual syrup was dissolved in chloroform (15 ml), silica gel (Kieselgel 60, 0.040–0, 063 mm) (2 g) was added and the suspension was strirred at 25°C for 6 h. Then silica gel was filtered off, washed with chloroform (3 × 3 ml), the filtrate was concentrated and crude **5b** was purified by silica chromatography using chloroform as the eluent. The fractions were checked by TLC and those containing the product were combined and evaporated. Yield 0.49 g, 49%. Anal. Found: B, 4.21; Br, 31.53. Calc. for $C_8H_{19}BBrNO_2$: B, 4.29; Br, 31.71%. In the case of **5c** the residue was suspended in ether (20 ml), filtered, the filter-cake was three times extracted with the filtrate, the extract was concentrated to a 10 ml volume, cooled to −80°C and the product was filtered off and dried. Yield 0.66 g, 63%. Anal. Found: B, 4.10; Br, 30.71. Calc. for $C_9H_{17}BBrNO_2$: B, 4.13; Br, 30.50%.

2.5.2. A.BH(Br)COOMe [A = Me_3N (5a), Q (5c)] from 1a and 1c with bromine in methanol

To a suspension of the amine-carboxyborane (4.0 mmol) in methanol (5 ml) a solution of bromine in

methanol (17.1 ml; 0.241 M) was added with vigorous stirring in a way that first 1 ml of the reagent–solution was added, and after 5 min the remaining portion was dropwise added over a period of 10 min. In the case of **5a** the procedure described at 2.5.1 was applied after waiting for 10 min. Yield 0.62 g, 73%. Anal. Found: B, 5.18; Br, 38.14%. For the preparation of **5c** the reaction mixture was treated, after 10 min, with quinuclidine (0.445 g; 4.0 mmol) and then it was evaporated to dryness. The residue was filtered with 15 ml of ether, the filter-cake was five times extracted with the filtrate, the extract was evaporated to dryness, suspended with *n*-pentane (10 ml), filtered, washed with *n*-pentane (3 × 2 ml) and dried. Yield 0.81 g, 77%. Anal. found: B, 4.13; Br, 30.62%.

*2.5.3. $Et_3N.BH(Br)COOMe$ (**5b**) from **2b** with NBS in chloroform*

To a stirred solution of **2b** (0.432 g; 2.49 mmol) in chloroform (15 ml) NBS (0.445 g; 2.50 mmol) was added, and after 10 min. the reaction mixture was extracted with cold (0°C) water (4 × 10 ml). The organic layer was separated, dried over Na_2SO_4 and evaporated to obtain the product **5b**. Yield 0.55 g, 88%. Anal Found: B, 4.34; Br, 31.75%.

2.6. Preparation of amine-dibromo(methoxycarbonyl)-boranes

*2.6.1. $A.BBr_2COOMe$ [A = Me_3N (**6a**), Q (**6c**)] from **4a** and **4c** in the presence of HCl catalyst in methanol*

A solution of the amine-dibromocarboxyborane (3.4 mmol) in methanolic HCl (30 ml; 0.1 M) was kept at 50°C for one week. In the case of **6a** the reaction mixture was evaporated to dryness, the residue was suspended in ether (10 ml), the solid material was filtered off and extracted ten times with ether (20 ml). The precipitate was filtered off and dried. Yield 0.80 g, 82%. Anal. Found: B, 3.71; Br, 55.45. Calc. for $C_5H_{12}BBr_2NO_2$: B, 3.74; Br, 55.34%. When preparing **6c** the product was precipitated upon cooling to room temperature, which was then filtered, washed with methanol (2 × 3 ml) and ether (2 × 3 ml) and dried. Yield 0.78 g, 67%. Anal. Found: B, 3.11; Br, 46.92. Calc. for $C_9H_{16}BBr_2NO_2$: B, 3.17; Br, 46.88%.

*2.6.2 $Me_3N.BBr_2COOMe$ (**6a**) from **2a** with bromine in methanol*

A solution of **2a** (0.44 g; 3.4 mmol) in methanol (20 ml) was mixed with a solution of bromine in methanol (42 ml; 0.17 M) at room temperature, allowed to stand for 12 h and then evaporated to dryness. The pale yellow residue was filtered using methanol (6 ml), washed with ether (5 ml) and then extracted eight times with ether (15 ml). The product, precipitated from the extract, was filtered, washed with ether (2 × 2 ml) and dried. Yield 0.46 g, 47%. Anal. Found: B, 3.69; Br, 55.28%.

*2.6.3 $Et_3N.BBr_2COOMe$ (**6b**) from **2b** with NBS in chloroform*

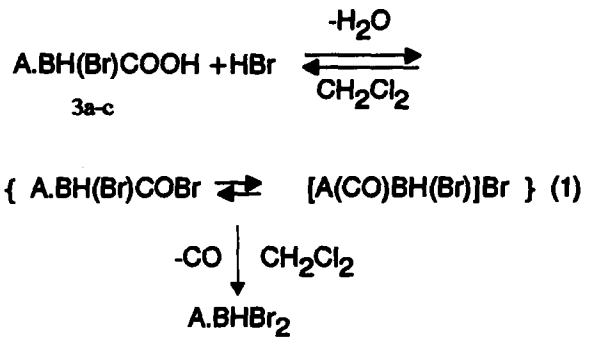
To a suspension of NBS (1.346 g; 7.56 mmol) in chloroform (5 ml) a solution of **2b** (0.436 g; 2.45 mmol) in chloroform (13 ml) was added. After 20 min the red solution was extracted with cold (0°C) water (5 × 10 ml) and the organic layer was dried over Na_2SO_4. Preparation of **6b** was then accomplished as described for **5b** at 2.5.1 with the difference that 6 h treatment with silica gel was omitted. Yield 0.40 g, 48%. Anal. Found B, 3.36; Br, 48.02. Calc. for $C_8H_{18}BBr_2NO_2$: B, 3.27; Br, 48.30%.

3. Results and discussion

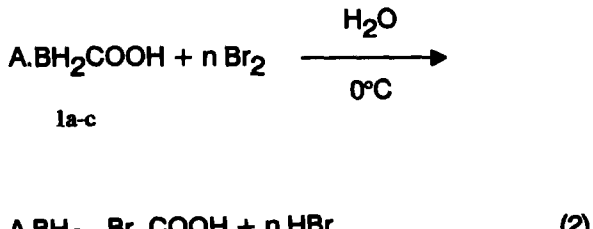
3.1. The reaction of amine-carboxyboranes with bromine, preparation, hydrolytic stability and spectral properties of amine-bromocarboxyboranes

The trimethylamine, triethylamine and quinuclidine complexes of carboxyborane (BH_2COOH) quickly react with a 1 molar equiv. of bromine in dichloromethane. The reaction gives rise to the evolution of 1 molar equiv. of CO, and the corresponding amine-complexes of $BHBr_2$ can be isolated with 50–60% yield. This process is explained by the formation of A.BH(Br)COOH and HBr in the first step, followed by decarbonylation of the bromo-carboxyborane complexes upon the action of HBr. The existence of this latter reaction was approved by treating amine-bromocarboxyboranes, obtained in an independent way, with HBr in CH_2Cl_2. (We have also shown that $Et_3N.BH_2COOH$ is decarbonylated with HBr in CH_2Cl_2 to afford $Et_3N.BH_2Br$ and CO in a ratio ca. 1:1.) The decarbonylation reaction proceeds most probably via the formation of an acid bromide derivative of bromocarboxyborane with HBr, which is in turn either decomposed directly with the evolution of CO, or first transformed into an amine-(carbon monoxide) boron(1 +) ion, from which CO is expelled by the bromide ion (Eq. (1)).

This assumption is supported by the finding that $Me_3N.BH(Br)COOH$ is also decarbonylated on the action of HCl or HI in CH_2Cl_2. The transformation with HCl is rather slow, leading to a 50% conversion over 40 h, and mainly $Me_3N.BH(Br)Cl$ is produced. At the same time the reaction with HI is as fast as that induced by HBr, and a nearly quantitative formation of $Me_3N.BH(Br)I$ is observed [2a]. Decarbonylation of carboxylic acids upon the action of acids is known [23] when a stable carbocation is formed by the loss of CO.



In proton–acceptor solvents (e.g. water, methanol, ether) the reaction of amine-carboxyboranes with bromine is accompanied by the liberation of a considerably smaller volume of CO. The trimethylamine complex of BH(Br)COOH and complexes of BBr_2COOH with each of the three examined amines could be obtained, with good yields, in an aqueous medium (Eq. (2)).



$$A.BH_{2-n}Br_nCOOH + n\,HBr \qquad (2)$$

3a, 4a-c

Treatment of $Et_3N.BH_2COOH$ and $Q.BH_2COOH$ with an equimolar amount of bromine in water led to a mixture containing the unchanged material and the dibromocarboxyborane complex in a 1:1 ratio. However, all of the three monobromocarboxyborane complexes could be prepared with good yields (77–94%) by means of bromination with NBS in chloroform.

As compared with that of $Me_3N.BH_2COOH$ [1] the hydrolytic stability of $Me_3N.BH(Br)COOH$ is considerably lower in acidic media, and it is dramatically decreased under neutral–alkaline conditions: the decomposition leads to a 1:1 mixture of H_2 and CO. To our best knowledge base-induced decarbonylation of carboxylic acids has not yet been reported. Gas-volumetric measurements clearly show that in buffered 1:4 methanol–water mixtures (pH = 0.2–7.2) at 25°C both the protonated and deprotonated acids are decomposed, and the half-lives for $Me_3N.BH(Br)COOH$ and for $Me_3N.BH(Br)COO^-$ are 160 min and 40 s respectively. The value determined for the protonated acid is further supported by ^1H NMR measurements in sulfuric acid, which also showed that up to a 5 M H_2SO_4 concentration the decomposition half-life is slowly increasing to ca. 6 h and then at 6.4 M it is decreasing to ca. 1 h. In HCl solutions of similar concentrations an extensive Br–Cl exchange also accompany the decomposition. In acidic media the produced $Me_3N.BH(Cl)COOH$ is much more stable than the corresponding bromo compound. By comparison of the results of our kinetic measurements with the data published in the literature [1] it is estimated that the H–Br exchange results in an acceleration of the decomposition with 2–3 and 8 orders of magnitude under acidic and neutral–alkaline conditions, respectively.

From the gas-volumetric measurements a value of pKa = 6.0 was obtained, which is smaller with ca. 2.5 than the value determined for $Me_3N.BH_2COOH$ [24]. Such a change in pKa is quite comparable with the ca. 2 units decrease arising from the α-bromination of carboxylic acids [25].

Decomposition of the triethylamine and quinuclidine complexes of BH(Br)COOH is similar to that of the Me_3N complex, but it is slightly faster in acidic media. The ^1H NMR studies have revealed that amine-dibromocarboxyboranes are much more stable than the corresponding monobromo compounds.

Comparison of the spectral data (Table 1) of the amine-bromocarboxyboranes with those of the amine-carboxyboranes [3,9,16] indicated that the bromo-substitution had resulted in an 80 cm^{-1} and 10 cm^{-1} shift of the ν(BH) and ν(CO) resonances, respectively, towards the higher wavenumbers and a downfield shift of the $\delta(^{11}B)$ values. All these data are in accord with the substitution of hydrogen with a more electronegative atom at boron. The UV $n \rightarrow \pi^*$ band of the C=O function appeared at 230–233 for $A.BH_2COOH$ and at 244–247 nm for A.BH(Br)COOH compounds. The 10–15 nm batochrome shift, due to bromination, corresponds to the shift arising from an α-halogen-substitution of acyclic carbonyl compounds. The anisochrony of the *N*-methylene protons in $Et_3N.BH(Br)COOH$ ($\Delta\delta = 0.022$ ppm) indicates that the configuration of the chiral boron atom is unchanged on the NMR time scale.

3.2. Synthesis of amine-(methoxycarbonyl)boranes, synthesis and properties of their bromo derivatives

Several methods have been reported [5,13,17,26,27] for the preparation of the esters of amine-carboxyboranes, of which the recent procedure of Morse and coworkers [13], involving esterification with orthoformates is quite attractive. We found that the aliphatic tertiary amine complexes of (methoxycarbonyl)boranes can also be conveniently prepared, with good yields, in methanol in the presence of a strongly acidic cation exchange resin (H^+ form) as the catalyst (Eq. (3)).

$$A.BH_2COOH + MeOH \xrightarrow[\text{reflux, 4-8 hours}]{\text{MeOH, resin}} A.BH_2COOMe + H_2O \quad (3)$$

1a-c 2a-c

resin = DOWEX AG 50 W

Such a procedure has been long employed for the esterification of carboxylic acids; most particularly in cases when mineral acids cause decomposition [28].

The methods useful for the preparation of the mono and/or dibromo derivatives of $A.BH_2COOMe$ are represented by Eqs. (4a–d).

Formation of the monobromo derivatives according to Eq. (4a) is very quick (a few minutes), whereas conversion into the dibromo analogues requires 2–10 h, and the yields are generally low due to extensive decomposition. Bromination and esterification can be achieved simultaneously, as illustrated by Eq. (4b), but sufficient yields can only be obtained with the monobromo compounds. Esterification of the dibromocarboxyborane complexes in methanol using HCl catalyst (Eq. (4c)) is very slow: the Me_3N and Q complexes could be isolated in good yields only in a one-week experiment at 50°C. Under the same conditions only a very small amount of $Et_3N.BBr_2COOMe$ could be prepared.

N-bromosuccinimide (NBS) was found to be conveniently employed for the synthesis of the triethylamine complexes of both the monobromo and dibromo (methoxycarbonyl)boranes (Eq. (4d)). The products were much more pure, and the yields were higher than in cases when bromination was carried out with elemental bromine (Eq. (4a)).

The synthesis of the bromo derivatives of pyridine base-carboxyboranes ($Pic.BH_2COOMe$ and $4\text{-}Me_2N\text{-}Py.BH_2COOMe$) [2a] failed either with bromine or NBS although quick consumption of the brominating agents occurred even at −50– − 80°C. Use of bromine in methanol resulted in decomposition accompanied by gas evolution on warming even when HBr was neutralized (pyridine-bases, $NaHCO_3$, NaOMe) at low temperature. No gas evolutin was observed on using NBS in $CHCl_3$, but separation of the multicomponent reaction mixtures remained unsuccessful.

Amine-monobromo(methoxycarbonyl)boranes possess a very low solubility in water, but are soluble in ether, THF, alcohols and in acetonitrile; $Et_3N.BH(Br)\text{-}COOMe$ is soluble even in benzene and *n*-pentane. The ester group of these derivatives undergoes fast hydrolysis under acidic conditions: the half-lives of the Me_3N, Et_3N and Q complexes in a 1 M HCl–MeOH (1 : 1) mixture are 90, 5 and 20 min, respectively. In alkaline medium the rate-determining step of the decomposition is the hydrolysis of the ester function; in a 0.2 M NaOH-MeOH (1 : 1) mixture the half-life is ca. 7 h for each of the three amine complexes.

The $\nu(CO)$ band of the methyl esters of aminebromocarboxyboranes appears at 20–25 cm^{-1} higher wavenumbers than those observed for the corresponding bromocarboxyborane complexes and this is in agreement with the tendency shown by the carboxylic

$$A.BH_2COOMe + n\,Br_2 \xrightarrow[n=1,2]{MeOH} A.BH_{2-n}Br_nCOOMe + n\,HBr \quad (4a)$$

2a-c 5a-c, 6a-c

$$A.BH_2COOH + n\,Br_2 + MeOH \xrightarrow[n=1,2]{MeOH} A.BH_{2-n}Br_nCOOMe + n\,HBr + H_2O \quad (4b)$$

1a-c 5a-c, 6a-c

$$A.BBr_2COOH + MeOH \xrightarrow[HCl]{MeOH} A.BBr_2COOMe + H_2O \quad (4c)$$

4a-c 6a-c

$$Et_3N.BH_2COOMe + n\,\text{(N-Br succinimide)} \xrightarrow[n=1,2]{CHCl_3} Et_3N.BH_{2-n}Br_nCOOMe + n\,\text{(N-H succinimide)} \quad (4d)$$

2b 5b, 6b

esters. In the ^1H NMR spectrum of $Et_3N.BH(Br)COOMe$ the $N-CH_2$ protons are anisochronic ($\Delta\delta = 0.008$ ppm), similarly to that observed for the analogous carboxy derivative. The stability of the enantiomers on the NMR time scale was demonstrated by the doubling of the OMe and NMe signals in the ^1H NMR spectrum of $Me_3N.BH(Br)COOMe$, when treating with europium optishift ($Eu(hfc)_3$) reagent.

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