SYNTHESIS AND PROPERTIES OF SOME ICOSAHEDRAL CARBORANE B,B′-DITHIOLS

Jaromír PLEŠEK, Zbyněk JANOUŠEK and Stanislav HEŘMÁNEK

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 250 68 Řež

Received November 7th, 1979

Reaction of icosahedral carboranes with excess sulfur over $AlCl_3$ converts in high yields *o*-carborane to 9,12-, and *m*-carborane to 9,10- and 5(4),9-dithiols which were transformed by CH_2Br_2 to the appropriate cyclic thioformal derivatives. Reaction of $9,12(HS)_2$-$1,2$-$C_2B_{10}H_{10}$ with acetone and $AlCl_3$ afforded a cyclic thioketal, the structure of which was confirmed by X-ray structure analysis. All structures were proposed on the ground of ^1H-, ^{11}B-NMR and mass spectra.

Recently we have described a synthesis of heteroborane-B-thiols based on the reaction of heteroborane with sulfur over aluminium chloride[1-6]. Exceptionally, a formation of small amounts of B,B′-dithiols has been observed in the reaction products. When following this secondary reaction we have found reaction conditions which have enabled laboratory-scale preparation of the B,B′-dithiols derived from icosahedral carboranes, especially from *o*-carborane ($1,2$-$C_2B_{10}H_{12}$, *I*) and from *m*-carborane ($1,7$-$C_2B_{10}H_{12}$, *II*). The optimum reaction conditions are shown in the Scheme 1:

$$\underset{1\ \text{equiv.}}{C_2B_{10}H_{12}} + \underset{3}{S} + \underset{4}{AlCl_3} \xrightarrow[160°C/8h]{\text{melt}} C_2B_{10}H_{10}(SH)_2\,. \qquad (I)$$

The reaction mixture contains a few by-products, namely the recently described 9-monothiols[1,2] and uncharged polysulfides resulting from the oxidation of primarily formed mono- and dithiols by an excessive amount of sulfur. In order to enhance the total yield of mercaptanes it was therefore recommended to reduce the alkali insoluble species by boiling with ethanol solution of sodium borohydride and to add the alkali soluble portion to the alkaline extract of the sulfhydrylation mixture. After acidification, the monothiols have been separated from the dithiols by chromatography on silica gel column or by crystallization.

o-Carborane (*I*) affords in the above way a very good yield of the $9,12(HS)_2$-$1,2$-$C_2B_{10}H_{10}$ dithiol (*Ia*), while the *m*-carborane (*II*) gives as a main product the dithiol $9,10(HS)_2$-$9,10$-$1,7$-$C_2B_{10}H_{10}$ (*IIa*), the structure of which resulted unambigously from the NMR and mass spectra, and a small amount of a second isomer (*IIb*) which is believed to be the $5,9(HS)_2$-$1,7$-$C_2B_{10}H_{10}$.

The electron density on particular BH vertices in *m*-carborane drops in the order B(9,10) > B(5,12) > B(4,6,8,11) > B(2,3)[4] which indicates also the order of the decreasing reactivity in sulfhydrylation. In agreement with this is the preferred formation of the $9,10(HS)_2$-$1,7$-$C_2B_{10}H_{10}$ derivative. The next isomer (according to the abudance) can be expected to be a compound with one HS-group in the position B(9), and with the second HS in one of the positions 4, 5 or 6. Of these, the 4,9- and 5,9- isomers have the HS groups in vicinal, and the 6,9-isomer in the *meta*-position. The alkylation with CH_2Br_2 yielded a monomer compound with the intramolecular —S—CH_2—S— bridge. This fact has eliminated the possibility of the 6,9-isomer which should give a polymer substance composed of the —(CH_2—S—$C_2B_{10}H_{10}$—S)-units.

TABLE I

Some Characteristics of Carboranethiols *Ia*, *IIa*, *IIb* and Their Derivatives *IIIa*, *IIIb*, *IIIc*, *IV*

Compound	Yield, % *m/e*	M. P., °C R_F[a]	^{1}H-NMR[b]			^{11}B-NMR[c]
			carborane —CH	—SH	other CH	
Ia	61·0 210	246—247 0·10	3·56 (2)	0·55	—	5·1
IIa	26·0 210	194—195 0·13	2·98 (2)	0·54	—	1·79
IIb	3·8 210	169—170 0·18	3·27 (1)	0·81	—	1·20
			2·90 (1)	0·57	—	−1·49
IIIa	90·3 222	265 (dec.) 0·06	4·14 (2)	—	3·67 (2)	
IIIb	84·4 222	154—156 0·09	3·33 (2)	—	4·41 (2)	5·2
IIIc	81·1 222	30—32 0·13	3·35 (1)	—	4·37 (2)	6·9
			2·97 (1)	—	—	4·2
IV	73·4 250	244—246 0·04	4·51 (2)	—	1·77 (6)	10·65

---

[a] On Silufol with benzene–hexane 1 : 1 as eluent; [b] in ppm relative to tetramethylsilane, $CDCl_3$ 60 MHz; intensities in parentheses; [c] singlets in ppm relative to $BF_3 . O(C_2H_5)_2$, lower field marked as + Shift in $CDCl_3$ at 32·1 MHz.

A preference of the $5,9(HS)_2$-$1,7$-$C_2B_{10}H_{10}$ isomer over the 4,9- one has resulted from the ^{11}B-NMR spectrum of *IIb* which shows signals at ppm (intensity, $^1J_{BH}$ in Hz): 1·20 (1, singlet), −1·49 (1, singlet), −5·34 (1, c. 165) −7·20 (1, 140), −11·2 (1, doublet), −13·25 (2, doublets), −14·7 (1, doublet), −17·62 (1, 184), −19·89 (1, 182). The fact that two signals in the highest field at −17·62 and −19·89 ppm have distinctly narrow width and large J_{BH} coupling constants allow to assign them to the B(3) and B(2) atoms which differ usually by these characteristics from other signals in *m*-carborane derivatives. The signal at −19·89 ppm belongs very likely to the B(2) atom due to the antipodal effect of the B(9) HS-group which shifts the signal of the opposite B(2) atom to the higher field.

Monomere cyclic thioformal derivatives $9,12(CH_2S_2)$-$1,2$-$C_2B_{10}H_{10}$ (*IIIa*) and $9,10(CH_2S_2)$-$1,7$-$C_2B_{10}H_{10}$ (*IIIb*) were analogously obtained from *Ia* and *IIa*. Dithiol *Ia* reacted in the presence of $AlCl_3$ also with acetone yielding thioketal $9,12[(CH_3)_2CS_2]$-$1,2$-$C_2B_{10}H_{10}$ (*IV*). Its crystal and molecular structures were established by the X-ray structure analysis[7] which confirmed and in detail defined the structure, suggested first on the ground of the NMR spectra. The characteristics of thioformal and thioketal derivatives are also given in Table I.

In the ^{1}H-NMR spectra only a slight splitting of H—S signal to a quartet with $^2J_{B-H}$ of c. 1 Hz was observed. In contrast to this, the signal of the CH_2 group in the thioformal derivatives *IIIa*–*IIIc* has shown a more distinct splitting which has the character of a heptet with $^3J_{BH}$ of c. 3 Hz. Both interactions are examples of a long-range B—S—H and B—S—$\underset{\text{H}}{\text{C}}$—S—B coupling which we have observed in a greater

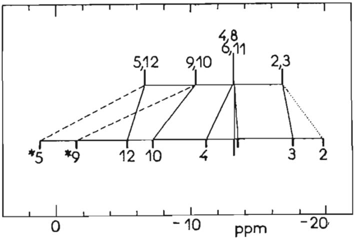

FIG. 1.

The Correlation Diagram of Schematized ^{11}B-NMR Spectra of $1,7$-$C_2B_{10}H_{12}$ (upper line) and of $X,9(HS)_2$-$1,7$-$C_2B_{10}H_{10}$ (bottom line) Showing the Chemical Shift Changes Brought by an Introduction of Two HS Groups

The best correlation fits with X = 5. The possibility X = 4 shows too great substitution shift for B(4) and no antipodal shift for B(11). Changes caused by the introduction of the HS group: the substituted vertex - - - - -, the antipodal vertex ············ .

or smaller extent with practically all derivatives having the B—S—CH_3 arrangement[2,6]. The detailed study of these interactions will be discussed elsewhere. A comparison of the ^1H chemical shift of the C—H vertex of dithiol *IIb* with that of dithiol *IIa*, and those of recently described 4- and 9-monothiols[1,2,4] allows to assign the signal at 3·35 ppm to the $C_{(7)}H$ vertex and the signal at 2·97 ppm to the $C_{(1)}H$ vertex. Similarly, the signal at 0·61 ppm belongs likely to the B(9)SH proton while that at 0·83 ppm can be assigned to the B(5)SH proton.

In ^{11}B-NMR spectra, the substitution of terminal H by SH group causes the change of a doublet to a singlet and the shift of 8 ± 2 ppm to the lower magnetic field. Similar shift-differences were observed with all described monothiols[1,2,4]. This fact is of a significant diagnostic relevancy for establishing the position of the introduction of the HS group not only with boranes but also with heteroboranes in general (Fig. 1).

Vicinal carboranedithiols *Ia*, *IIa*, *IIb* are now relatively easily accessible. It allows the development not only of the chemistry of their complexes with heavy metals but also of the general reactions of B,B′-vicinal dithiols, which could be of interest from the medicinal standpoint.

EXPERIMENTAL

Mass spectra were determined with a LBK 9000 instrument at 70 eV. The ^1H (100 MHz) and ^{11}B (32·1 MHz)-NMR spectra were recorded using a Varian XL-100 spectrometer, the ^1H-NMR spectra at 60 MHz were measured with Tesla BS 467 spectrometer. Melting points were determined in a Koffler block and are uncorrected.

Carboranedithiols

A mixture of 14·4 g of carborane *I* (or *II*), 9·3 g of sulfur and 52 g of $AlCl_3$ was during one hour heated to 160°C and maintained at this temperature for 8 h. The mixture melted at c. 130°C. By standing overnight, the yellow melt was dissolved under initial cooling in 300 ml of ethanol and the turbid solution was poured off from the lump excess sulfur into 1 000 ml of water. The separated crude product was sucked off, dissolved in 200 ml of benzene, the solution was filtered and extracted by 3 . 50 ml of 10% potassium hydroxide. The extract containing carboranethiols was left aside as a fraction A. Benzene layer, containing beside 10—15% of unreacted starting carborane *I* (or *II*) mainly the carborane polysulfides, was evaporated *in vacuo*. Carborane *I* (or *II*) was then recovered by the sublimation at 13 Pa/100°C (bath).

To the sublimation remainder, composed of a rich mixture of carborane B-polysulfides[1], was added 200 ml of ethanol, 4·0 g of sodium hydroxide and 1·0 g of sodium borohydride, and the resulting mixture was boiled till all solid species dissolved (c. 1 h). The solution was concentrated *in vacuo* to 100 ml, poured into 400 ml of water and filtered. The clear filtrate was combined with the above alkaline fraction A, the solution was saturated with carbon dioxide and the separated products were extracted into 3 . 50 ml of benzene. After evaporation *in vacuo*, a crude mixture of carboranethiols was sublimed at 13 Pa/140°C (bath). The pure compound *Ia* (12·7 g, 61%) was obtained from the sublimate by twice repeated crystallization from hot cyclohexane. In parent liquors, mainly 9-monothiol[1,2] remained beside a small amount of dithiol. The mixture of both compounds can be easily separated by the chromatography on a silica gel column.

In the case of *m*-carborane, the sublimate containing a mixture of thiols was dissolved in a minimum amount of benzene–hexane 1 : 2 mixture, poured onto a column of 200 g of silica gel and eluted using the same solvent system. By stepwise elution, combination of fractions containing individual compounds, evaporation, and subsequent sublimation *in vacuo* were obtained 6·1 g (35·6%) of 9-monothiol[1,2], 0·8 g (3·8%) of dithiol *IIb* and 5·4 g (26%) of dithiol *IIa*.

Thioformal Derivatives *IIIa–IIIc*

To the solution of 1·0 g dithiol (*Ia*, *IIa* or *IIb*) in 50 ml of ethanol was added 1·0 g of potassium hydroxide and 1·0 g of CH_2Br_2. After 1 h standing at room temperature, the mixture was heated to boiling and left again to cool. The mixture was then poured into 300 ml of 5% aqueous potassium hydroxide, and the separated product was extracted into 3 . 20 ml of benzene. The extract was filtered, the solvent evaporated *in vacuo* and the remainder crystallized from the hot benzene–cyclohexane 1 : 1 mixture with *IIIa* or *IIIb*. The compound *IIIc* was – due to its low m.p. – only washed with hexane at −10°C. In all cases, the yields exceeded 80%.

Dimethyl Thioketal *IV*

To the solution of 4·0 g of dithiol *Ia* in 50 ml of acetone was under cooling to 0°C gradually added 10 g of $AlCl_3$ and the mixture was left to stand for 4 days. The suspension of a solid compound in a brown solution was then poured into 200 ml of water, the product was filtered, washed by 2 . 10 ml of ethanol, dried, and crystallized from boiling benzene. Compound *IV* started to separate slowly from the cool filtrate in the form of slightly yellow prisms which were filtered after two days; 3·5 g (73·4%). Crystals from this preparation were used for the X-ray diffraction study, ref.[7].

The mass spectra were measured by Dr J. Mitera, the ^{11}B-NMR *spectra by Mr P. Pech, Prague Institute of Chemical Technology. The* ^{1}H-NMR *spectra were recorded by Dr F. Mareš, Institute of Inorganic Chemistry, Czechoslovak Academy of Science, Řež. All these colleagues are thanked for their assistance.*

REFERENCES

1. Plešek J., Heřmánek S.: Chem. Ind. (London) *1977*, 360.
2. Plešek J., Heřmánek S.: This Journal *43*, 1325 (1978).
3. Plešek J., Heřmánek S.: This Journal, in press.
4. Plešek J., Heřmánek S.: This Journal, in press.
5. Janoušek Z., Plešek J., Plzák Z.: This Journal *44*, 3010 (1979).
6. Plešek J., Janoušek Z., Heřmánek S.: This Journal *43*, 1332 (1978).
7. Šubrtová V., Línek A., Hašek V.: Acta Cryst., in press.

Translated by the author (S. H.).