SYNTHESIS AND PROPERTIES OF 1-HSCH$_2$-1,2-C$_2$B$_{10}$H$_{11}$

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Synthesis of 1-HSCH$_2$-1,2-C$_2$B$_{10}$H$_{11}$ from B$_{10}$H$_{12}$(SR)$_2$ and (CH$_3$)$_3$C—SCH$_2$C≡C is described. A distinctly greater difference in acidity at the couple C$_6$H$_5$SH/1-HS-1,2-C$_2$B$_{10}$H$_{11}$ (ΔpK_a 4·20) in comparison with the couple C$_6$H$_5$CH$_2$SH/1-HSCH$_2$-1,2-C$_2$B$_{10}$H$_{11}$ (ΔpK_a 2·34) confirmed the great significance of a "mesomeric acidification" of the HS-group bound to a carborane framework.

For the study of the relationship between pK_a values of mercaptocarboranes and the electron density in the vertices before substitution[1] we have needed as a comparative compound a mercaptocarborane in which the HS-group is separated from the carborane nucleus by the CH$_2$-group. In such a compound, the pK_a value of the HS-group should not be influenced by a mesomeric stabilization of the formed C—$\underline{S}|^{(-)}$ anion with the carborane framework. As an optimum compound 1-HSCH$_2$-1,2-C$_2$H$_{10}$H$_{11}$ (*I*) was elected that has not been described up to present. Its synthesis was accomplished according to the Scheme 1.

$$B_{10}H_{12}(S(C_2H_5)_2)_2 + (CH_3)_3CSCH_2C{\equiv}CH \xrightarrow[4\ h]{\text{toluene, } 80°C}$$

$$1(CH_3)_3CSCH_2\text{-}1,2\text{-}C_2B_{10}H_{11} \xrightarrow[50°C,\ 10\ min]{AlCl_3,\ \text{benzene}} 1\text{-}HSCH_2\text{-}1,2\text{-}C_2B_{10}H_{11}$$

II 51% *I* 87%

Scheme 1

Compounds *I* and *II* are crystalline substances. ^{1}H and ^{11}B NMR spectra of compound *I* and mass spectra *m/e* of *I* and *II* were in agreement with the expected structures.

Potentiometric titration of *I* in 50% ethanol–water mixture showed the pK_a value of 8·40. The value is considerably high for a substituted aliphatic mercaptan when compared with the acidity of benzyl mercaptan which has under identical conditions the pK_a value of 10·74. The distinctly higher acidity of *I* can be explained by a strong inductive effect of the 1-*o*-carboranyl group. This effect is known[2] and it is connected with an outstanding positive charge on the C-atom in the *o*-carborane. In comparison with this, the acidity of compound *I* is by five orders lower than that of 1-HS-1,2-

-$C_2B_{10}H_{11}$ (pK_a 3·30) (ref.[1,3]) where the mercapto group is directly bound to the skeletal C-atom. The great difference (pK_a 5·10) is hard to be explained by a decrease in the inductive effect due to the incorporation of the —CH_2-group between the carborane C-atom and the HS-group in *I*. It is obvious that the outstanding acidity of *III* is to a large extent evoked by the mesomeric stabilization of the C—$\overline{S}|^{(-)}$ anion, *i.e.* by a dissipation of a part of the electron density into the carborane framework. This effect cannot apply with compound *I*. Such a "mesomeric acidification" is well known in organic chemistry where it causes an increase in the acidity of thiophenols by approximately three orders in comparison with aliphatic mercaptans. In agreement with this we have found under analogous conditions the pK_a values of 10·74 for benzyl mercaptan, 7·60 for *p*-tolyl mercaptan and 7·50 for phenyl mercaptan.

EXPERIMENTAL

Mass spectra were determined with a LKB 9000 instrument at 70 eV, ^1H (100 MHz) and ^{11}B (32·1 MHz) NMR spectra were recorded in $CDCl_3$ using a Varian XL-100 spectrometer. Potentiometric titrations were performed in the ethanol–water mixture (1 : 1 v/v) with 0·1M-NaOH as the titrant. TLC was carried out on Silufol (silica gel on Al foil, Kavalier, Votice, Czechoslovakia). Benzyl mercaptan[4] and *p*-tolyl mercaptan[5] were prepared according to the cited literature

Synthesis of 1-$(CH_3)_3CSCH_2$-1,2-$C_2B_{10}H_{11}$ (*II*)

Propargyl terc-butyl sulfide was prepared from 10·1 g (0·06 mol) of terc-butylthiuronium chloride in 100 ml of 10% aqueous solution of potassium hydroxide by shaking with 7·1 g (0·06 mol) of propargyl bromide for 10 min at 40°C. The product was steam distilled *in vacuo*, water layer was saturated with solid potassium hydroxide and the upper layer was used without any further purification as propargyl terc-butyl sulfide. The crude sulfide was added to the solution of 18·0 g (0·06 mol) of $B_{10}H_{12}(S(C_2H_5)_2)_2$ in 150 ml of toluene and the mixture was heated under nitrogen at 80°C for 4 h. Evolution of hydrogen stopped after 3 h. Toluene was evaporated *in vacuo*, the remainder was extracted with 3 . 30 ml portions of hexane and the combined extracts were separated on the column of 200 g of silica gel using benzene–hexane (1 : 2) as the eluent. Fractions were checked by TLC and those containing compound *II* were collected, solvents evaporated *in vacuo* and the product crystallized from hot hexane, yielding 7·5 g (51%) of crystals which can be sublimed at 100°C and 13 Pa (0·1 Torr); m.p. 101—102°C, R_F 0·45 (TLC, benzene–hexane 1 : 2), *m/e* 248 corresponds to $^{12}C_7{}^{11}B_{10}{}^{32}S^1H_{22}$.

Preparation of 1-$HSCH_2$-1,2-$C_2B_{10}H_{11}$ (*I*)

To the solution of *II* (5·0 g, 0·02 mol) in 50 ml of benzene was added 4·0 g (0·03 mol) of anhydrous $AlCl_3$ during 10 min under shaking. The temperature raised spontaneously and its color turned orange-brown. After the addition of the last portion and after shaking for additional 5 min the mixture did not contain starting compound *II* according to the TLC. Under cooling, the mixture was diluted with 50 ml of water, the benzene layer was separated, washed with 50 ml of 10% hydrochloric acid, then with water, and extracted with 3 . 50 ml of 10% KOH solution.

The alkaline extract was saturated with carbon dioxide and extracted with 2 . 30 ml of hexane, the solvent evaporated *in vacuo* and the residue sublimed at 70°C (bath) and 13 Pa (0·1 Torr). Yield 3·3 g (87%) of compound *I*, m.p. 55°C, *m/e* 192 in agreement with $^{12}C_3{}^{11}B_{10}{}^{32}S_1H_{14}$; R_F 0·37 (TLC, benzene–hexane 1 : 2). ^{1}H-NMR spectrum of *I* showed signals at 1·86 (SH), 3·30 (CH_2) and 4·12 (CH) ppm (relative to tetramethylsilane). ^{11}B-NMR spectrum exhibited following doublets (intensities): —3·3 (1), —6·0 (1), —9·5 (2) and —13·2 (4) ppm (relative to $BF_3.O(C_2H_5)_2$, — sign specifies the shift to the higher field) from which the first three doublets can be assigned to $B_{(9)}$, $B_{(12)}$ and $B_{(8,10)}$. The ^{11}B-NMR spectrum corresponds well to a C-substituted *o*-carborane.

Potentiometric Titrations

Studied compound (0·01 mol) dissolved in 50 ml of ethanol was diluted with 50 ml of water and immediately titrated potentiometrically with 0·1%-NaOH in 50M ethanol at room temperature. Following pK_a values were found: benzyl mercaptan 10·74, *p*-tolyl mercaptan 7·60, phenyl mercaptan 7·50, compound *I* 8·40.

Mass spectra were measured by Dr V. Kubelka, ^{1}H *and* ^{11}B-NMR *spectra by Mr P. Pech, Prague Institute of Chemical Technology, Prague.* pK_a *values were determined by Mr M. Skalický and Mr M. Filip, Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řež. We would like to express out thanks to these colleagues for their assistance.*

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