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REACTION OF 6,9-BIS(DIALKYL-SULFIDO)DODECAHYDRODECABORANES WITH MERCURIC SALTS

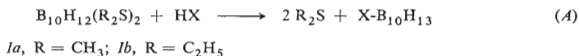
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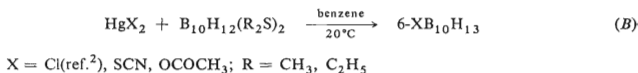
The reaction of 6,9-bis(dialkylsulfido)dodecahydrodecaboranes with mercuric salts, leading to 6-substituted decaborane derivatives, is described. By this synthesis 6-isothiocyano and 6-acyoxydecaboranes were prepared which were inaccessible by previous preparative methods.

In previous communications¹⁻³ we have described a new reaction, *i.e.* the transformation of 6,9-bis(dialkylsulfido) dodecahydrodecaboranes (*I*) to monosubstituted derivatives of decaborane. This reaction takes place between the molecule of compound *I* and strong anhydrous acids in benzene as medium. During the addition of the acid to the $B_{10}H_{12}L_2$ molecule the expulsion of both ligands takes place under the formation of decaborane derivatives substituted in the position 5 and 6.



The reaction did not proceed in the presence of weak acids (organic acids, hydrogen sulfide, and hydrogen cyanide), probably because they are unable to bind the dialkylsulfide set free during the reaction.

We found now that some mercuric salts which are known to be capable of forming strong coordination compounds with dialkyl sulfides, react with compounds of the



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type *I* under formation of 6-substituted decaboranes even in the absence of a free acid in the reaction mixture.

The position of the substituent was determined on the basis of IR spectra by a method elaborated in our institute⁴, and by means of ¹¹B NMR spectra.

The transformation according to the equation (*B*) does not take place either in the presence of mercuric cyanide or bromide, or in the presence of diphenylmercury. Mercuric iodide reacted under formation of a complex mixture of compounds in which 6-dialkylsulfidododecahydrodecaborane (*II*) prevailed. Mercuric fluoride reacted with compounds *I* under partial oxidative degradation of the starting compound and the formation of compound *II* which was detected only chromatographically. The formation of compound *II* can be explained in both cases by the splitting off of one molecule of the ligand by the mercuric salt.

The mechanism and the stereochemistry of the formation of substituted decaboranes during the mentioned transformations are not sufficiently clear. Reduction of the bivalent mercury to monovalent mercury² (in the case of mercuric chloride) or to elementary mercury in the case of the use of mercuric acetate or thiocyanate evidently takes place. We assume that the corresponding acid is set free during the reduction which then reacts with the excess of compound *I* according to equation (*A*). In this the

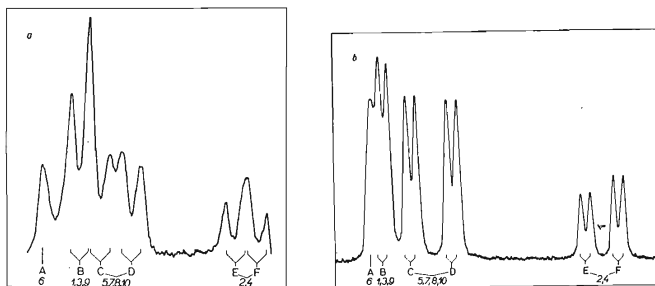


FIG. 1

¹¹B NMR Spectrum

a) of 6-acetoxydecaborane in benzene at 32.1 MHz. A singlet 1.1 p.p.m.; B doublet 11.3 p.p.m. (151 c.p.s.); C doublet 16.5 p.p.m. (200 c.p.s.); D doublet 25.2 p.p.m. (154 c.p.s.); E doublet 53.5 p.p.m. (170 c.p.s.); F doublet 61.4 p.p.m. (166 c.p.s.).

b) of 6-isothiocyanodecaborane in carbon disulphide at 80.2 MHz, A singlet 9.6 p.p.m.; B doublet 11.9 p.p.m. (153 c.p.s.); C doublet 17.2 p.p.m. (172 c.p.s.); D doublet 24.7 p.p.m. (180 c.p.s.); E doublet 51.5 p.p.m. (175 c.p.s.); F doublet 57.1 p.p.m. (175 c.p.s.).

mercuric salt enhances the reaction in the required direction by binding the eliminated dialkyl sulfide. This supposition finds appreciable support in the fact that on addition to free acetic acid during the reaction with mercuric acetate the yield is substantially increased, because in this case the losses of the starting material caused by oxidation are less. The described reaction is presently the only method of preparation of substituted decaboranes which cannot be obtained by conventional methods, *i.e.* by direct substitution of decaborane under the conditions of Friedel-Crafts reaction⁵ or by the addition of acids to 6,9-bis(dialkylsulfido)dodecahydrodecaboranes¹⁻³.

¹¹B NMR spectrum of acetoxytridecahydrodecaborane at 32.1 MHz (Fig. 1a) shows singlet in the lowest field which indicates the substitution in position 6. This fact is also confirmed by splitting of 2, 4 and 5, 7, 8, 10 doublets⁶.

The spectrum of isothiocyanotridecahydrodecaborane at 32.1 MHz was less informative but at 80.2 MHz was well resolved and indicated clearly 6-substitution (Fig. 1b). This spectrum is very interesting because of unusually large distance between doublets of boron atoms 2 and 4, resp. 5, 7 and 8, 10. On the basis of the corresponding difference in electronegativity and on the basis of the IR spectra of the compound 6-NCSB₁₀H₁₃ (Fig. 2) we prefer the latter of the two possible structures (thiocyano and isothiocyano derivative).

The strong doublet at 1242 or 1274 cm⁻¹ resp., can be assigned to the B—N stretching vibration. Sowerby⁷ gives the values 1308 and 1344 cm⁻¹ (inflexion) in B(NCS)₃ for this vibration. The diminution of the frequencies in our case can again be explained by the suppression of the pseudo-multiple character of the B—N bond as mentioned above. Antisymmetric stretching vibration NCS is represented by the band at 2080 cm⁻¹ with a complex structure on the branch at lower frequencies. This structure was also observed by certain authors⁸ who, however, had no plausible

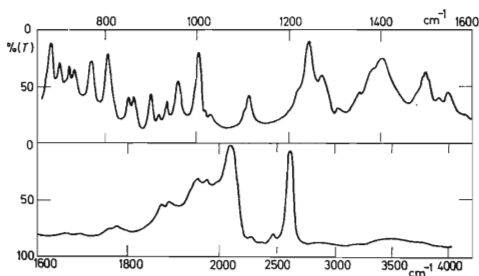


FIG. 2

Infrared Spectrum of 6-Isouthiocyanodecaborane

interpretation for it. The strong band at 807 cm^{-1} can be assigned with great probability to the stretching vibration of C—S (ref.⁹) and the band at 505 cm^{-1} of medium strength to the bending vibration of NCS (ref.¹⁰). We were unable to identify the symmetric stretching vibration of the NCS group, due probably to its superposition with the bands of the decaborane skeleton at 1002 or 956 cm^{-1} . Similarly to the preceding case the presence of the band at 1403 cm^{-1} is probably indicative of the substitution in the position 6, in accordance with the ^{11}B NMR spectra. Other points that are indicative of the substitution in the position 6 are the appreciable strengthening of the band at 1002 cm^{-1} and the characteristic positions of the bands at 681 , 719 , and 733 cm^{-1} . The stretching vibration of the terminal B—H bonds appears as bands at 2588 cm^{-1} and 1970 cm^{-1} . Their intensity is striking and it could indicate a possible migration of the substituent into the bridge position.

In the spectrum of 6-AcOB₁₀H₁₃ (Fig. 3) the band at 1737 cm^{-1} and the inflexion at 1756 cm^{-1} are due to the antisymmetric stretching vibration of the C=O group, and the band at 1186 cm^{-1} to the C—O stretching vibration. Bands at 1323 and 1209 cm^{-1} can be assigned to the stretching vibration of B—O. These frequencies are substantially lower than in esters of alkylboric acids where the frequency values are around 1300 – 1400 cm^{-1} . In our case this decrease can be explained by the suppression of the pseudomultiple character of the B—O bond in consequence of the sp^3 hybridisation of the atom B₍₆₎ to which the acetoxy group is bound. In accordance with the ^{11}B NMR spectra we can infer from the presence of the band at 1424 cm^{-1} in the region of bridge bending vibrations B—H—B that it is a 6-substituted decaborane¹¹. This is also corroborated by the appreciable strengthening of the band at 1006 cm^{-1} and the characteristic position⁴ of the bands at 690 , 705 , 722 ,

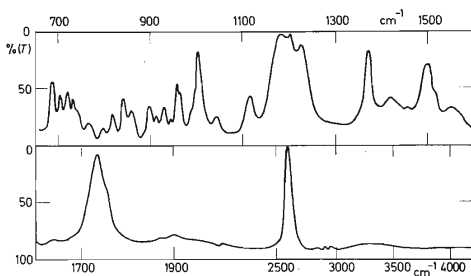


FIG. 3
Infrared Spectrum of 6-Acetoxydecaborane

and 733 cm^{-1} . The band at 1372 cm^{-1} is due to the symmetric bending vibration of CH_3 , while the maxima at 2979 cm^{-1} can be assigned to the symmetric stretching vibrations. In the region of stretching vibrations of the bridge hydrogens very weak bands at 1870 and 1901 cm^{-1} can be assigned to these vibrations. The frequency of the stretching vibration of terminal B—H is 2582 cm^{-1} .

EXPERIMENTAL

All operations connected with the isolation of the products were carried out in the standard vacuum apparatus, unless stated otherwise. Melting points are not corrected. They were determined in sealed capillaries and under nitrogen. ^{11}B NMR spectra of 6-isothiocyano and 6-acetoxycycloborane were measured at 32.1 and 80.2 MHz, $\text{B}(\text{OCH}_3)_3$ being used as external standard. Infrared spectra were measured on a two-beam spectrophotometer UR 10 (Jena), using 5% solutions in carbon disulfide or carbon tetrachloride.

6-Isothiocyanotridecahydrodecaborane

a) From 6,9-bis(dimethylsulfido)dodecahydrodecaborane (Ia): To a suspension of 11.1 g (0.035 mol) of mercuric thiocyanate in 100 ml of benzene 4.3 g (0.018 mol) of compound Ia were added and the mixture was occasionally shaken and allowed to stand overnight. During the standing a precipitate of mercury was formed while the supernatant was strongly yellow. The reaction mixture was filtered and the precipitate was washed with benzene. The filtrate was concentrated and the residual oil was extracted with pentane. The crude product was sublimated at $60^\circ\text{C}/10^{-5}$ Torr in a sublimation stick cooled to 0°C . Yield 0.7 g (22.2%) of thiocyanotridecahydrodecaborane, m.p. $83\text{--}85^\circ\text{C}$. The sample for analysis was crystallized from pentane. For $\text{B}_{10}\text{H}_{13}\text{NCS}$ (179.4) calculated: 60.32% B, 17.87% S, 7.81% N; found: 59.47% B, 17.33% S, 7.44% N.

b) From 6,9-bis(diethylsulfido)dodecahydrodecaborane (Ib): To a solution of 13.65 g (0.045 mol) of compound Ib in 200 ml of benzene 14.45 g (0.045 mol) of mercuric thiocyanate were added and the mixture was allowed to stand under occasional shaking for 3 days. The black precipitate formed was filtered off and washed with benzene. After evaporation of benzene the product was isolated as in the preceding experiment. Yield 0.75 g (9.1%) of thiocyanotridecahydrodecaborane which was identified by comparison of its IR spectrum.

6-Acetoxytridecahydrodecaborane

a) To a solution of 4.2 g (0.017 mol) of compound Ia in 200 ml of benzene 5.5 g (0.017 mol) of mercuric acetate were added gradually under cooling with water and occasional shaking. After 2 hours standing the black precipitate was filtered off and washed with benzene. The yellow benzene filtrate was evaporated *in vacuo* and the residue was extracted with pentane. The residue after evaporation of pentane was sublimated at $50^\circ\text{C}/10^{-5}$ Torr. The sublimate was dissolved in boiling pentane and the solution was allowed to crystallize freely. The separated crystals were freed from mother liquor and dried at $20^\circ\text{C}/10^{-2}$ Torr. Yield 0.2 g (6.5%) of acetoxytridecahydrodecaborane, m.p. $138\text{--}140^\circ\text{C}$. For $\text{B}_{10}\text{H}_{13}\text{OCOCH}_3$ (180.4) calculated: 59.66% B, 13.32% C, 8.95% H; found: 59.7% B, 13.01% C, 8.75% H.

b) To a solution of 6 g (0.235 mol) of compound Ia in 200 ml of benzene 10 ml of glacial acetic were added followed by gradual addition (over one hour) of 8 g (0.025 mol) of mercuric acetate (stirring and cooling). After two hours the mixture was filtered, the solid material on the

filter of sintered glass was washed with benzene and the filtrate was evaporated and extracted with a mixture of pentane and benzene 2 : 1. The extract was concentrated and the formed crystals were extracted with boiling pentane in a continuous extractor. From the extract 0.9 g of product crystallised out which was dried at $20^{\circ}\text{C}/10^{-2}$ Torr. Mother liquors were concentrated to dryness and the residue sublimated at $50^{\circ}\text{C}/10^{-5}$ Torr to give another 0.1 g of product. Total yield 1 g (22.2%). The identity of both crops with acetoxytridecahydrodecaborane from the preceding experiment was proved by IR spectroscopy. The residue from the reaction mixture which was insoluble in the pentane-benzene mixture was extracted with 40 ml of dichloromethane and the extract was added with 50 ml of ether. This caused the precipitation of 2.6 g (43.3%) of the starting material, *Ia*, identified chromatographically on a thin layer of silica gel.

c) To a solution of 6.4 g (0.021 mol) of compound *Ib* and 3 ml of glacial acetic acid in 150 ml of benzene 6.8 g (0.021 mol) of mercuric acetate were added gradually under stirring and cooling. After 3 hours the precipitated mercury was filtered off and the filtrate was evaporated to dryness and extracted with benzene-pentane 1 : 5. The extract was evaporated to dryness and the residue was extracted with boiling pentane in a continuous extractor. From the extract separated 1.4 g (35.5%) of acetoxydecaborane, identical according to IR spectral data with the product obtained under *b*).

Neutralization of Isothiocyano- and Acetoxytridecahydrodecaborane

The weighed sample was dissolved in 200 ml of 50% ethanol and an excess of a 0.2M-NaOH solution was added to the solution. After 15 minutes phenolphthalein was added and the excess of the base was retitrated with 0.2M-HCl. For the neutralization of one equivalent of thiocyanotridecahydrodecaborane 2.12 equivalents of sodium hydroxide were consumed, while for the neutralisation of acetoxytridecahydrodecaborane 2.3 equivalents were necessary. The change of the colour of the indicator was not sufficiently sharp.

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