After a third of a century in organoboron chemistry

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Abstract - Following a summary of some earlier work, recent results achieved in the field of organo-boranes will be elucidated. A variety of organoboron reagents have now attained important positions in the palette of reagents used by chemists in many fields of research. The success in transforming information gained from analytical surveys on a range of organic compounds using organoboron reagents to new and interesting types of reactions and/or organoboranes, justifies the prediction that other novel boron specific applications will be found on this basis. Knowledge gained from this type of approach will further our understanding of structure, bonding and reaction pathways. It seems probable that future work with organoborons will also bring many more impulses to chemistry.

Early in 1952 I began working on aluminium organic compounds under the guidance of Karl Ziegler at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr (ref. 1,2). Many new applications were being found for organoaluminium compounds which were, at that time, considered to be laboratory curiosities. These investigations in Mülheim led to their world-wide usage in industry and research.

OUR INVESTIGATIONS OVER 30 YEARS

The Mülheim organoboron chemistry in the 50's

In view of the importance of Ziegler's pioneering work it therefore seemed interesting to ascertain the differences and similarities between aluminium and boron chemistry. Right at the start of this work, we could apply the displacement reaction ("Verdrängungsreaktion") known for the aluminiumtrialkyls to the reactions of trialkylboranes with alkenes, alkadienes and alkatrienes (ref. 3). The exchange of boron and aluminium substituents was also used to prepare new organo boron- and organo aluminium compounds (ref. 4). It was also found that the non-catalyzed hydrogenation of B-C-bonds with H_2 under pressure gives alkyldiboranes(6) and diborane (ref. 3,5).

$\rangle$BH borane additions to C=C bonds (ref. 6,7) were realised using alkyldiboranes(6) and mainly tri-ethylamine-borane (ref. 4). A large number of new organoboron compounds could be prepared with the aid of thermal borylation (ref. 7-9). Examples of some of these are shown in Fig. 1 and 2.
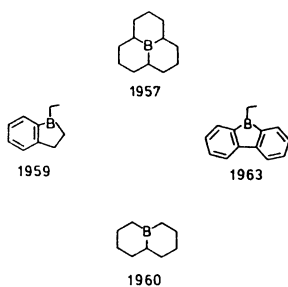

Fig. 1. Cyclic triorganoboranes through C=C-hydroborations and thermal CH-borylations
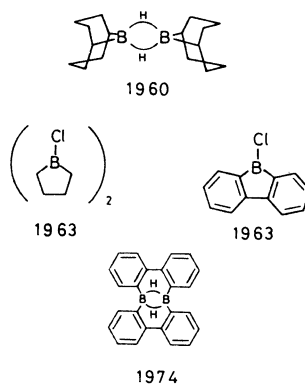

Fig. 2. Cyclic organodiboranes(6) and chloroboranes

Cyclic organoboron compounds having BC_3- (ref. 6,8,9), BC_2H- (ref. 10) and BC_2Cl-groupings (ref. 11,12) resulted. (9-BBN)$_2$ has found wide-spread usage in synthesis and analysis. The cyclic BN-compounds shown in Fig. 3 were also prepared using new methods at the start of the 1960's (ref. 13). Hydroboration was used in an analogous manner to Ziegler's hydroalumination, to prepare alkylboranes at the start of our investigations. Thermal cyclizations were used to prepare new aliphatic (G.W. Rotermund) and aromatic (with K. Reinert) triorganoboranes. The study of the alkyl/hydride exchange reactions led to the first cyclic organodiboranes(6) (ref. 10).
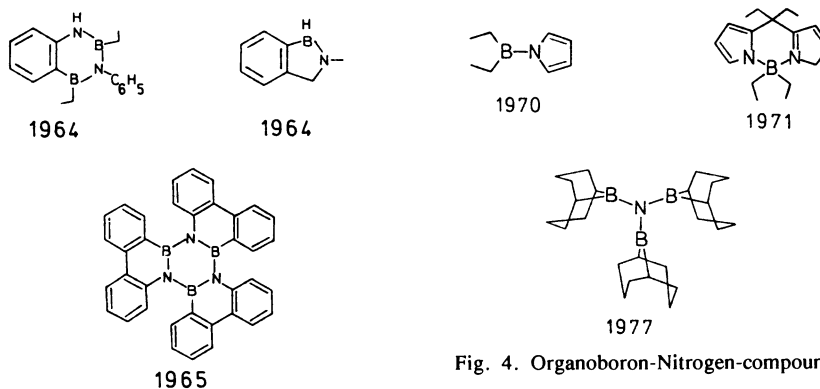

1964   1964   1970   1971

1977

1965

Fig. 4. Organoboron-Nitrogen-compounds through N-borylation and condensation

Fig. 3. Organoboron-Nitrogen-compounds through thermal borylation

Novel organoboron—nitrogen chemistry

The chemistry of organopyrrolylboranes (ref. 14) was investigated together with H. Bellut. New condensation products with e.g. diethylketone could be prepared (ref. 15). The crystalline compound with the previously unknown triborylated nitrogen atom (ref. 16) was made preparatively available by G. Seidel using substitutions of N-Lithium intermediates; cf. Fig. 4.

The first B-organocarboranes

In the 60's we also found a completely new route to B-alkylcarboranes: G.W. Rotermund hydroborated ethynylboranes and obtained the first peralkylated closo-C_2B_3-carboranes (ref. 17). Shortly thereafter M.A. Graßberger carried out the alkali-metal dehalogenation of alkyl-halo-boranes which led to new B-alkylated nido-(CB$_5$) and closo-(C$_2B_5$)carboranes (see Fig. 5) (ref. 18). In 1984 the pentaalkyl-C_2B_3 carborane was used to prepare the first C_4B_6-carboranes (ref. 19) as the peralkylderivative.
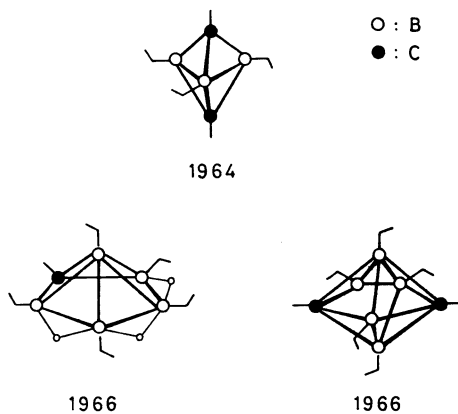

O : B
● : C

1964

1966   1966

Fig. 5. B-Organocarboranes of closo- and nido-type

A useful borane-specific rearrangement

Since 1965 together with P. Binger a new boron-specific synthesis of a large variety of substituted al-
kenes was investigated. This popular synthetic approach involves the reaction of 1-alkinylborates with
electrophiles and the C-C coupling regioselectively yields new organic compounds. In many cases only
one stereoisomer is formed; cf. Fig. 6 (ref. 20). Examples of the compounds prepared using this method
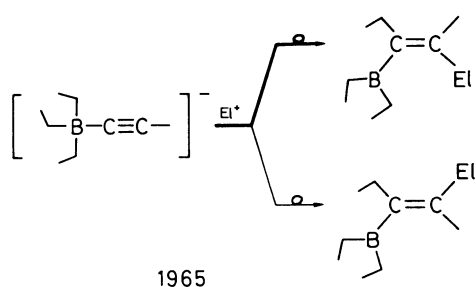are shown in Fig. 7 (ref. 21-24).
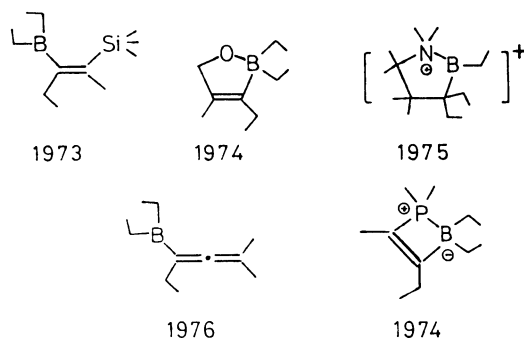
Fig. 6. Borylalkenes from alkinylborates

Fig. 7. Products of the addition/rearrangements of
alkinylborates with electrophiles

A new aprotic oxidation method

Together with Y. Morita we have published in 1966 an useful oxidation method for organoboranes (cf.
Fig. 8). BC-bonds can be partially, completely and sometimes selectively be transformed to BOC-bonds
using trimethylamine N-oxide. This method is also excellently suited for the quantitative determination of
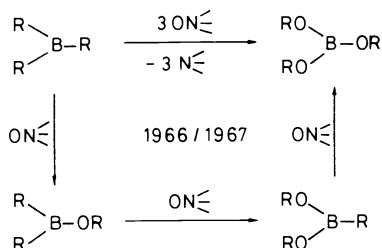BC-bonds (ref. 25).

Fig. 8. BC-Oxidations with trimethyl-
amine-N-oxide

More specific transformations with organoboron reagents

At the end of the 60's W. Fenzl achieved a new C-C coupling method using vinyloxyboranes (ref. 26).
The BOC=C-grouping can add to nitrile- and carbonyl functions (cf. Fig. 9).   These reactions are in
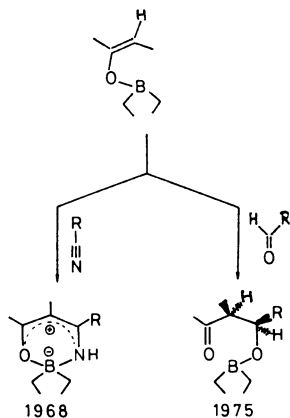some cases highly stereoselective, cf. Fig. 10 (ref. 27-29).

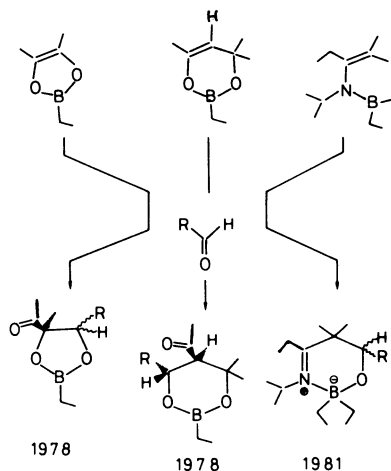Fig. 9. Vinyloxyborane additions to multiple bond systems

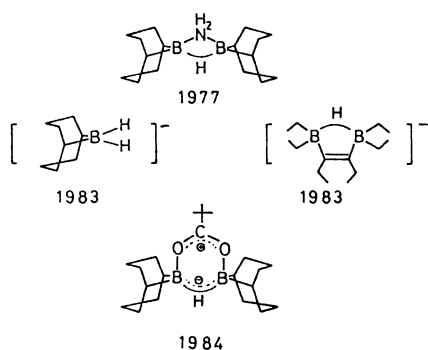Fig. 10. Aldol addition products from vinyloxyborane

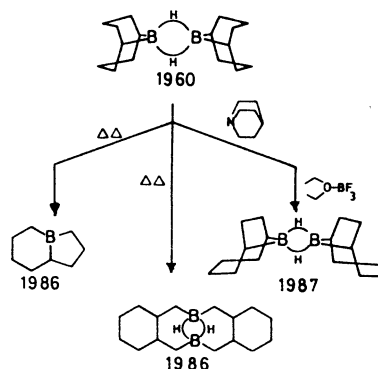Fig. 11. Organoboron compounds with hydride substituents

Fig. 12. $C_8H_{15}B$-Isomers from Bis(9-borabicyclo-[3.3.1]nonane)

Unusual organoboronhydrides

For many years we had been involved in reductions using $\diagdown$BH organoboranes and -borates. Some of the new BH compounds having interesting structures are shown in Fig. 11. 1,5-Cyclooctanediyl borates were investigated by G. Seidel. The six membered ring compound (ref. 31), which was found by P. Idelmann, is of importance for understanding the reductions of carboxylic acids.

In connection with some applications of (9-BBN)$_2$ reactions at temperatures higher than 130°C we have tested the thermal behaviour of the borabicyclo[3.3.1]nonane ring in the condensed states and also in the gas phase (ref. 32). M. Yalpani has found, that three different isomerizations of the $C_8H_{15}B$ system can occur (Fig. 12).

New organoboron heterocycles

Syntheses of a large series of new heterocycles containing one or two boron-atoms were be realised in the last years together with G. Seidel (ref. 33). The heterocycles shown in Fig. 13 (ref. 34) can be synthesized starting from cis-3,4-bis(diethylboryl)-3-hexene, which was first prepared in 1966 (ref. 35).

Fig. 14 shows some new cyclic compounds prepared in good yields from 3-diethylboryl-2-trimethylsilyl-2-pentene.
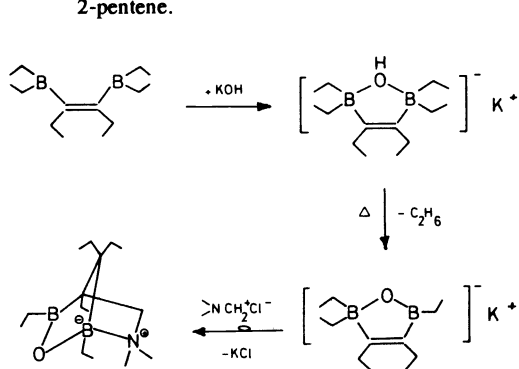
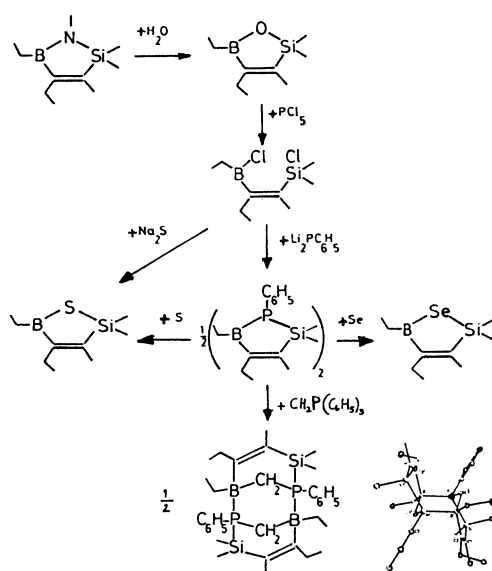Fig. 13. $\diagdown$BOB$\diagup$-Heterocycles from 1,2-diboryl-alkenes

Fig. 14. Boron-Element-Silicon-Heterocycles from 1,2-silyl-boryl-alkenes. The X-ray structure was performed by R. Boese, University of Essen.

Analytical tests with organoboron reagents

With the help of organoboron compounds a large number of organic compounds have either been prepared for the first time or become more accessible. Organoboranes and -borates are interesting for analytical investigations. Both activated triethylborane and various alkyldiboranes(6) are well-suited reagents enabling analytical tests. The so called EZ, HZ values are determined (ref. 36). These give indications for achieving reactions such as partial and catalysed ⟩BH borane reductions.

Some transformations in the chemistry of ethylboron oxygen compounds

In the course of our analytical investigations together with W. Schüßler it was found that trifluoroacetic acid is only reduced to the aldehyde stage by R_2BH-compounds. The resulting 16-membered ring compound (cf. Fig. 15) behaves as an acetal which is not reduced by ⟩BH boranes.
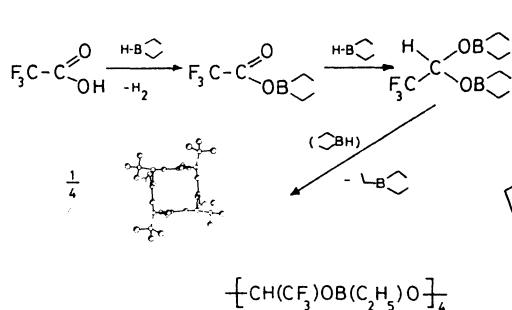

$$\left[CH(CF_3)OB(C_2H_5)O \right]_4$$

Fig. 15. ⟩BH-borane reduction of trifluoroacetic acid to the 16-membered ring, X-ray structure determined by R. Boese, University of Essen.
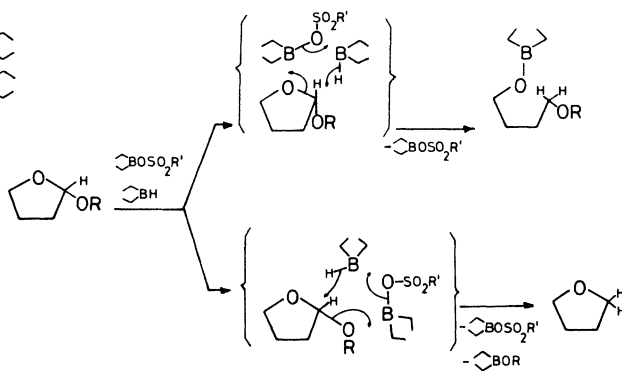
Fig. 16. Catalyzed ⟩BH-borane reduction of acetals, shown here for furan derivatives.

It was also found in our analytical probing, that both acetals and glycosides can be reduced to the ether stage (ref. 37) by hydroboration in the presence of certain catalysts such as 9-methanesulfonato-9-BBN (MSBBN) (cf. Fig. 16).

Together with W.V. Dahlhoff it was found, that beside the cycloamyloses the catalyzed reduction with ⟩BH-organoboranes leads to new preparative applications. Both amylose and cellulose can be regioselectively reduced to give the novel polymer poly-1,4-anhydro-D-glucitol (cf. Fig. 17) (ref. 38).

Generally, when using ⟩BH organoboranes for the reductions of carbohydrates, the Et_2B- or EtB⟨-protective groups can play important roles (cf. Fig. 18) (ref. 39).

Fig. 17. Poly-1,4-anhydro-D-glucitol
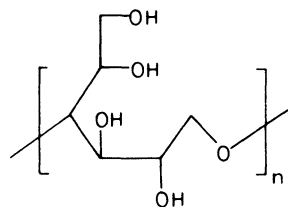
D-Mannitol 1976

D-Mannose 1980

2-Deoxy-D-ribose 1982
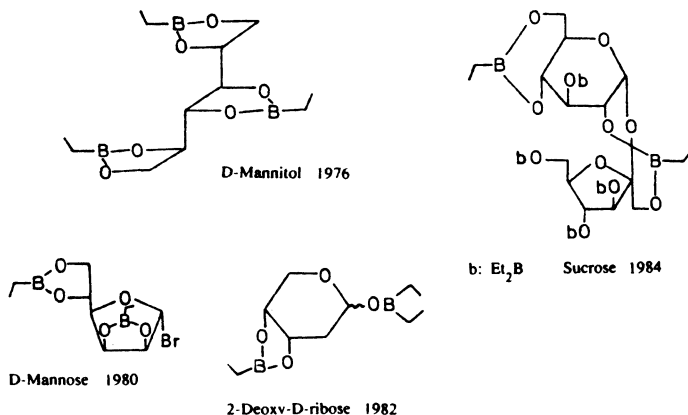
b: Et_2B Sucrose 1984

Fig. 18. O,O'-Ethylboranediyl protected polyhydroxy compounds

An interesting investigation carried out by W.V. Dahlhoff demonstrated that the ethylboron-protective groups can be introduced with eg. activated triethylborane or with triethylboroxin (cf. Fig. 19,20) (ref. 40,41) under very mild conditions.
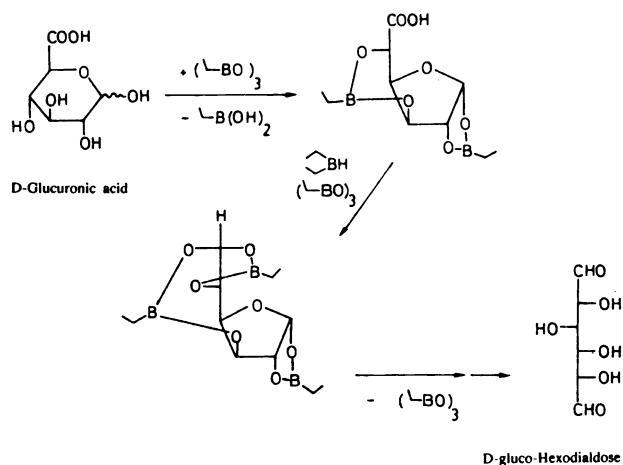

Fig. 19. D-gluco-Hexodialdose from D-glucuronic acid

The reduction of D-glucuronic acid to D-gluco-hexodialdose (cf. Fig. 19) or of D-glucurono-6,3-lactone to L-gulose and D-gluco-hexodialdose (cf. Fig. 20) are only possible with organoboron compounds. The reactions occur in high yields and they represent the best methods for preparing these two saccharides (ref. 41).
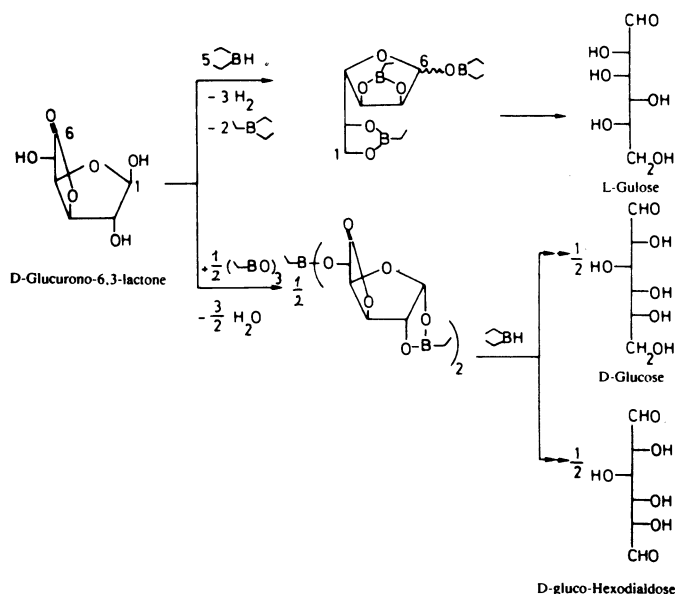

Fig. 20. L-Gulose, D-glucose and D-gluco-hexodialdose from D-glucurono-6,3-lactone

The generation of free aldehydo groups in certain polyhydroxy hemiacetals using ethyl-dimethoxy-borane is an example of a boron specific reaction (cf. Fig. 21) (ref. 42).

The finding of the organoboron-model for the Fischer-Tropsch-Synthesis together with M. Yalpani (ref. 43) was also based on our analytical investigations (cf. Fig. 22). Using this model the steps in the Fischer-Tropsch-Synthesis can be better separated and understood. Further, the model offers new possibilities for testing novel and modified catalyst systems.
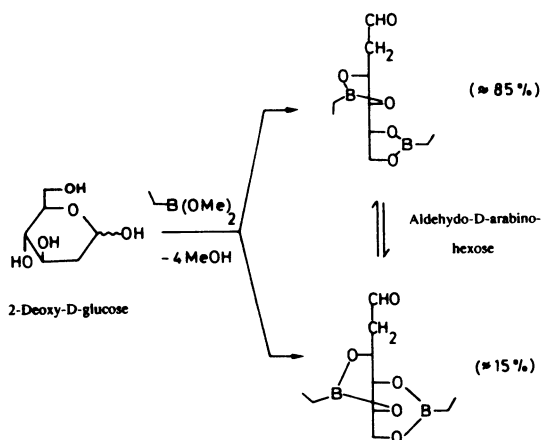
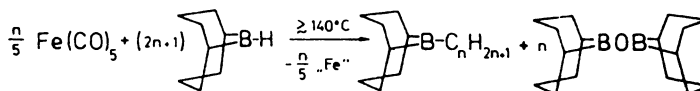Fig. 21. Aldehydo-D-arabino-hexose from 2-deoxy-D-glucose

Fig. 22. Organoboron model of the Fischer-Tropsch-Synthesis

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