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ORGANOBORANES IN SYNTHESIS AND ANALYSIS

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Abstract - Organoboranes which are important for preparative purposes include triethylborane, alkyldiboranes and in particular diethylborylpivalate and bis-(ethylpivaloyloxy)diboroxane (BEPDIB). - Several new boron-specific applications of organoboranes in synthesis of organic compounds will be given. Tri- and tetrasubstituted (Z/E)-alkenes are sometime obtained highly selectively on reaction of heteroatom containing electrophiles with substituted 1-alkinylborates. - Versatile aldol-additions and both homo- and mixed condensations of ketones and certain aldehydes can be carried out with the help of organoboranes. - Stereoselective formation of erythro- and threo-ketoles can be performed using the easily obtainable vinyloxyboranes. - Separations, purifications and selective O-derivatisations of polyhydroxy compounds are possible via O-ethylboranediyl derivatives. The O-ethylboron protective groups are useful for the NMR-spectroscopic identification of polyalcohols, saccharides and their derivatives.

INTRODUCTION

During this symposium many novel boron compounds will be described, some of which have interesting properties. The emphasis is, however, on the mode of formation and the bonding involved. Possible applications of boron compounds are often neglected, although their organic derivatives have become important in the synthesis of organic compounds during the past 20 years.

Hydroboration has become a key reaction in many synthetic routes involving both the introduction of functional groups and the formation of new C-C-bonds. The hydroboration reaction has been quite thoroughly investigated. One knows the regio-, stereo- and enantioselectivities of the BH addition and one can apply this reaction usefully in organic syntheses. The resumée is that organoboranes and -borates often have specific properties in synthesis and analysis which are not usually shown by other classes of compounds. Hydroboration has opened up a great field of new synthetic possiblities as can be seen in the large number of monographs and also in certain text books. You will, therefore, understand why I do not wish to talk about this reaction today. Instead, I will deal with some new observations and some other specific applications of organoboranes.

THE TOPICS

The boron compounds themselves are not the centre point of our research, instead we are more concerned with what can be done with these compounds, i. e. the full-title of the talk should be: "Some possible applications of organoboranes in the synthesis and analysis of organic compounds".

The following reactions are examples of the uses of organoboranes in synthesis:
1. The preparation of multiply-substituted alkenes from and via organoborates.

2. The stereoselective synthesis of erythro and threo ketols and alkanediols from and via dialkyl-substituted vinyloxyboranes.

3. Homo and mixed condensation reactions of carbonyl compounds with the help of certain organoboranes.

4. The regioselective O-derivatization of alkanepolyols and carbohydrates.

The examples of the analytical applications involving organoboranes include the following topics:
1. The purification and separation of polyhydroxy compounds using organoboranes.

2. The quantitative determination of water and hydroxyl groups in both organic and inorganic compounds.

3. The use of the ethylboron-protective group for the spectroscopic identification of natural products and other organic compounds.

I would like to discuss some of these topics today. All of these methods involve the use of simple organoboron compounds. Triethylborane, ethyl- and propyldiboranes(6), as well as certain BO-compounds such as diethylboryl-pivalate, bis(ethyl-pivaloyloxy)diboroxane (BEPDIB) and ethylboroxine are involved. I hope that those who expected descriptions of boron compounds with interesting new structures will not be disappointed. Special structures and properties only result on reaction with the organic substrates. We have, however, been able to prepare many new intermediates and endproducts which can only be obtained by using the element boron. Most of the reactions which I will describe proceed smoothly and yield very pure products.

HETEROATOM SUBSTITUTED VINYLBORANES

About 12 years ago we first described a synthetic route to multiply substituted alkenes (Ref.1). It is based on the reaction of triorgano-1-alkynylborates with electrophiles. This reaction, which involves addition and rearrangement, has received much attention. Some of the results which have been obtained using this reaction are shown in Fig. 1.

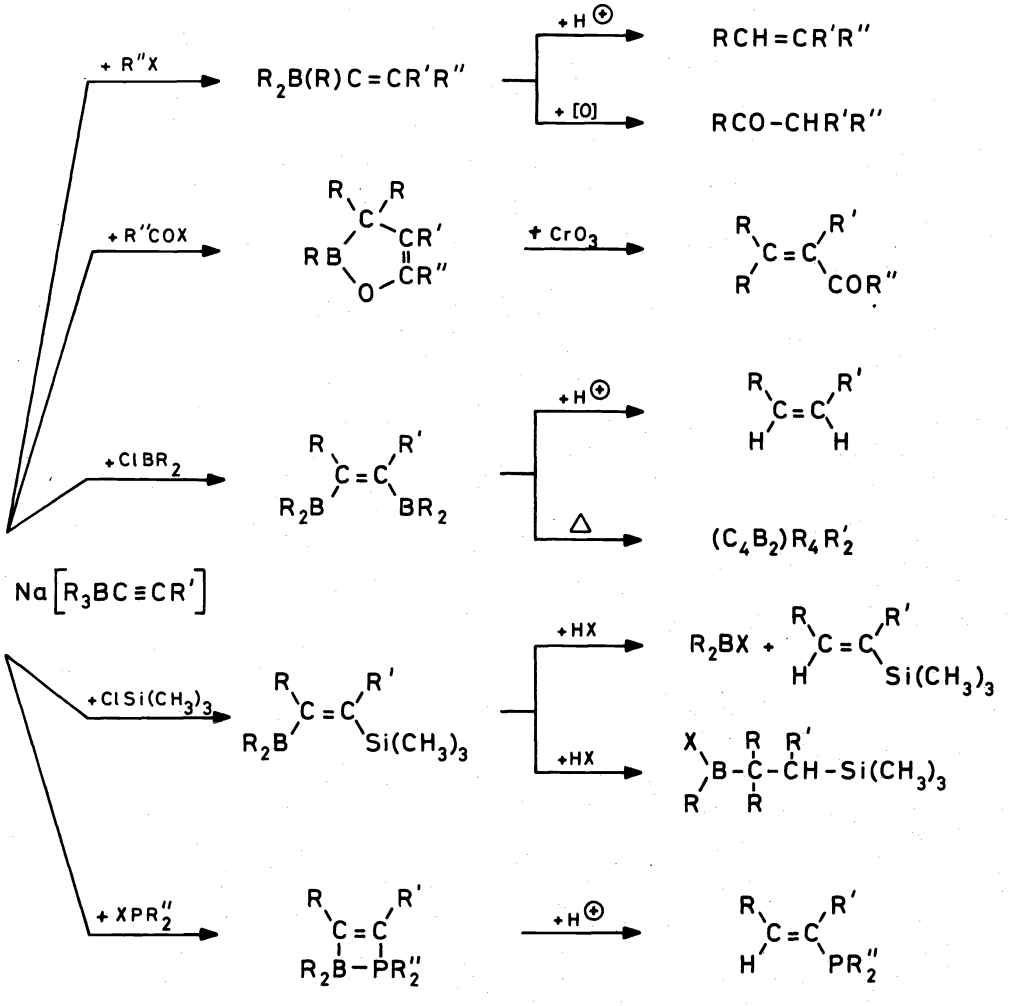

Fig. 1. Reaction products from 1-alkynylborates via substituted vinylboranes

I will concentrate on the stereoselectivity of this reaction which depends on the substituents which are presents and on the groups which are to be introduced at C^2. The lack of stereoselectivity of some of these reactions has sometimes hindered their development as a useful synthetic reagent. The hydrolysis of the rearranged borates - the substituted vinylboranes - usually produces mixtures of (E)- and (Z)-alkenes. Several methods have been developed to overcome the lack of stereoselectivity of the reactions, such as destruction of the geometrical integrity of the alkene by oxidation of the dialkylvinylboranes to ketones (Ref. 2). Some reactions e.g. with acylchlorides are used to cause further alkyl group migration (Ref. 3). An additional approach involves the use of certain functional groups [$Et_2B^{\oplus}$(Ref. 4) $SiMe_3^{\oplus}$(Ref.5) and $P(C_6H_5)_2^{\oplus}$ (Ref.6) as electrophiles] within the organoborate to direct the reaction to only one specific isomer. Facile separation of the two isomers is sometimes possible; e.g. in the cases of the methoxymethylelectrophile or in the reverse case with the triethyl-3-methoxy-1-propynylborate (Ref. 7). Using both ways one obtains the two isomers.

The reaction of sodium triethyl-1-butynylborate with the electrophilic dimethylmethyleneammoniumbromide also leads to two isomers (Ref. 8). Sodium-3-dimethylamino-1-propynylborate, however, reacts with triethyloxoniumtetrafluoroborate to give a substituted ammonium-borate, this is because the electrophilic addition takes place on the nitrogen atom (Ref. 8).

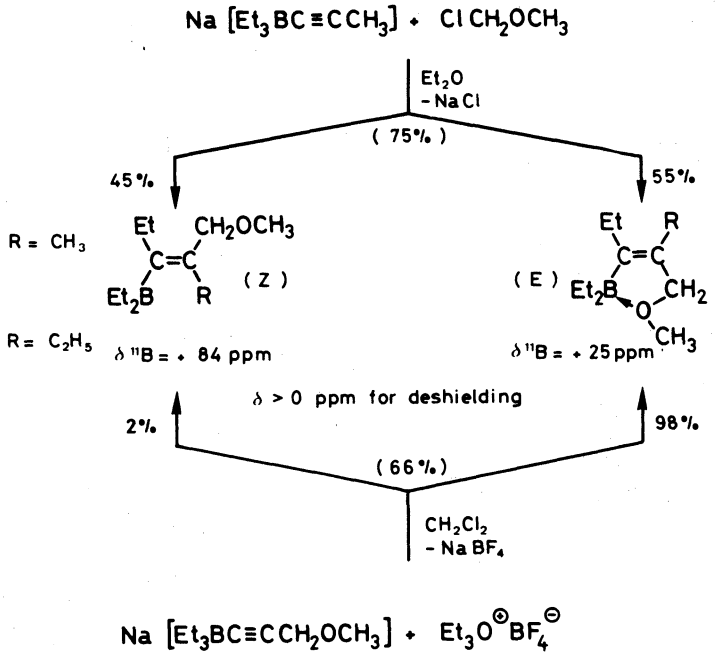

Fig. 2. The formation of (Z/E)-2-methoxymethylvinylboranes

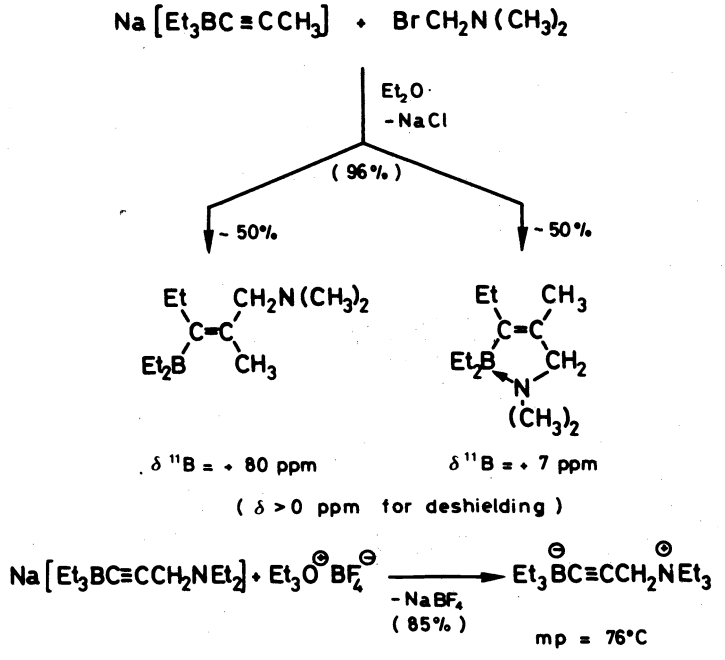

Fig. 3. The different reaction pathways of the dimethylaminomethyl-derivatives

The same reactions are given in Fig. 4 for sodium-triethyl-trimethylsilylethynylborate (Ref. 9).

In this case the stereoselectivity of the addition/rearrangement to the alkenes is much higher. The influence of the silicon-atom seems to be very important. Usually the reactions with 2-trimethylsilyl-ethynylborates lead mainly to one isomer: with $Et^{\oplus}$, $^{\oplus}CH_2NMe_2$, $^{\oplus}CH_2OMe$, $^{\oplus}P(C_6H_5)_2$ one obtains one major product. For example, a crystalline 1,2-phosphaboret-3-ene is formed from sodium-triphenyl-2-trimethylsilylethynylborate and diphenyl-chlorophosphane (Ref. 9). The structure of the 1,2-phosphaboret-3-ene was determined by x-ray analysis (C. Krüger, MPI für Kohlenforschung, Mülheim-Ruhr).

Trimethylsilylethynylborate, however, reacts less selectively with chlorodiethylborane or with acetylchloride (Ref. 9). The competition of the trimethylsilyl- and the diethylboryl groups toward the triethylboron-substituent is evident. Both isomers are formed, but one isomer rearranges.

The acetyl addition gives a nearly equimolar mixture of the two isomers. Only the (E)-isomer, however, is isolable; this on heating rearranges to the (Z)-isomer which in turn rapidly forms the silylated 1,2-oxaborolene-(4) after a second ethylgroup migration from the B-atom to the C^1-atom.

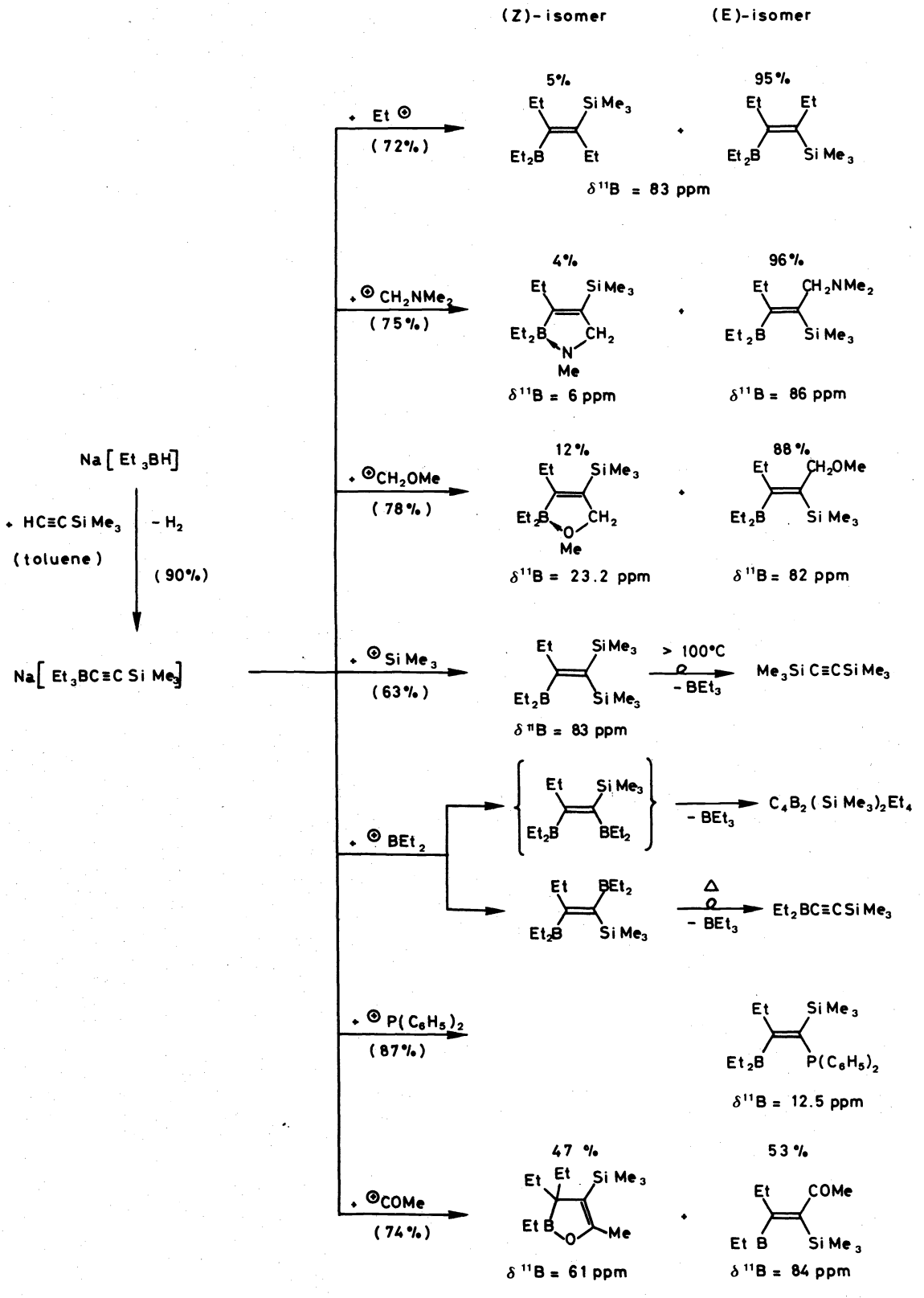

Fig. 4. The influence of silicon on the formation of (Z/E)-tetrasubstituted alkenes via 1-alkynylborates

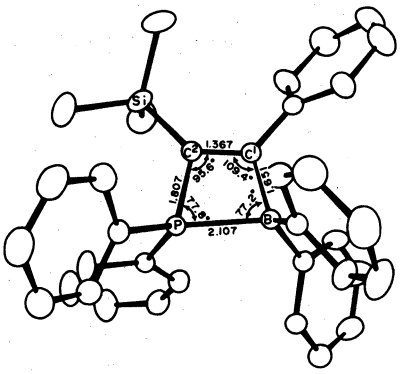

Fig. 5. X-ray structure of 1,1,2,2,3-pentaphenyl-4-trimethylsilyl-1,2-phosphaboret-3-ene (Ref. 9)

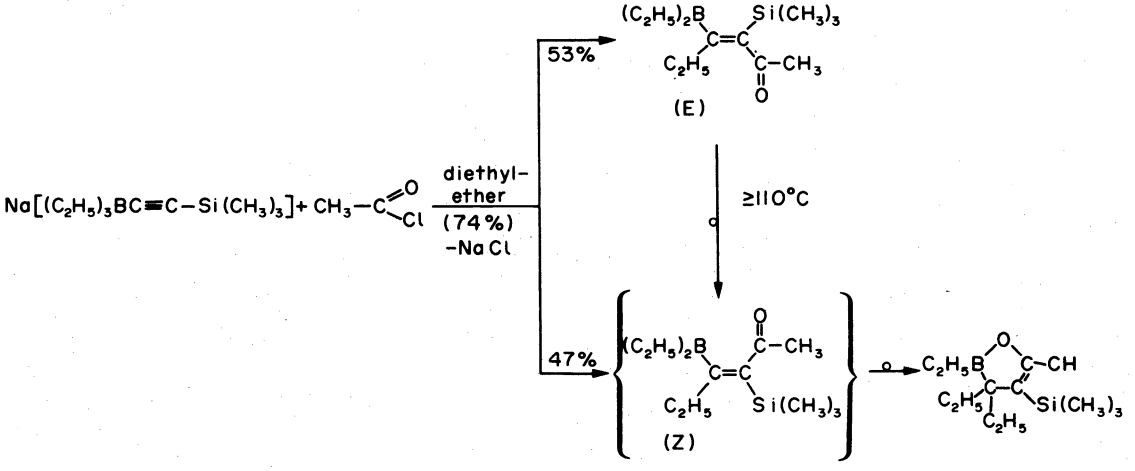

Fig. 6. The acetylation of sodium-triethyl-2-trimethylsilyl-ethynylborate

The influence of silicon in further reactions of the borylated tetrasubstituted ethylene is also evident in the case of hydroxysubstituted compounds.

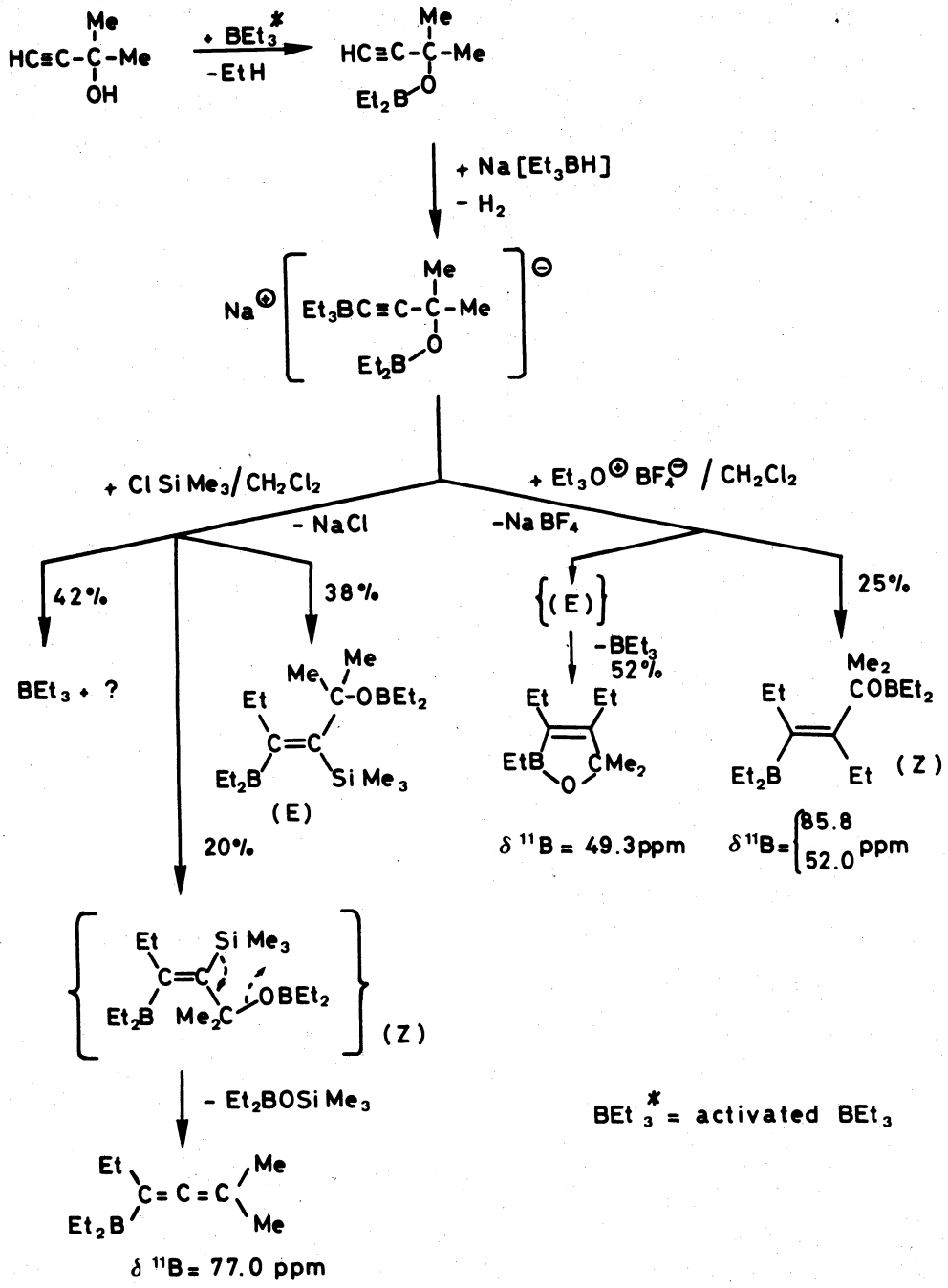

Fig. 7. Derivatization of 3-alkinols via an O-borylated 1-alkynylborate

After the diethylborylation of 3-methylbutinol and the transformation into the borate one obtains various end products on reaction with a trimethylsilyl-electrophile (Ref. 10). Beside triethylborane (42 %) and the normal (E)-isomer (38 %) an allenic borane can be isolated in pure form. We assume, that the (Z)-isomer is an allene precursor, which eliminates diethyltrimethylsilyloxyborane very easily. The ethylation of this borate on the other hand leads to two compounds: the stable (Z)-isomer (25 %) and a 1,2-oxaborolene-(3) (52 %), which is propably formed after BEt_3-elimination from the (E)-isomer (Ref. 10).

The next example of a borate/electrophile combination shows the influence of the migrating group. Sodium triphenyl-3-methyl-3-buten-1-ylborate and sodium triethyl-3-methyl-3-buten-1-ylborate react with the triethyloxonium-tetrafluoroborate to give different types of end products (Ref. 10). Whereas the ethyl compound leads to an equimolar mixture of the (Z/E)-vinylborane, the phenyl derivative yields a Wurtz-product (15 %) and a boron heterocycle which must have formed from the original (E)-isomer by migration of a second B-phenylgroup to the C^1-atom.

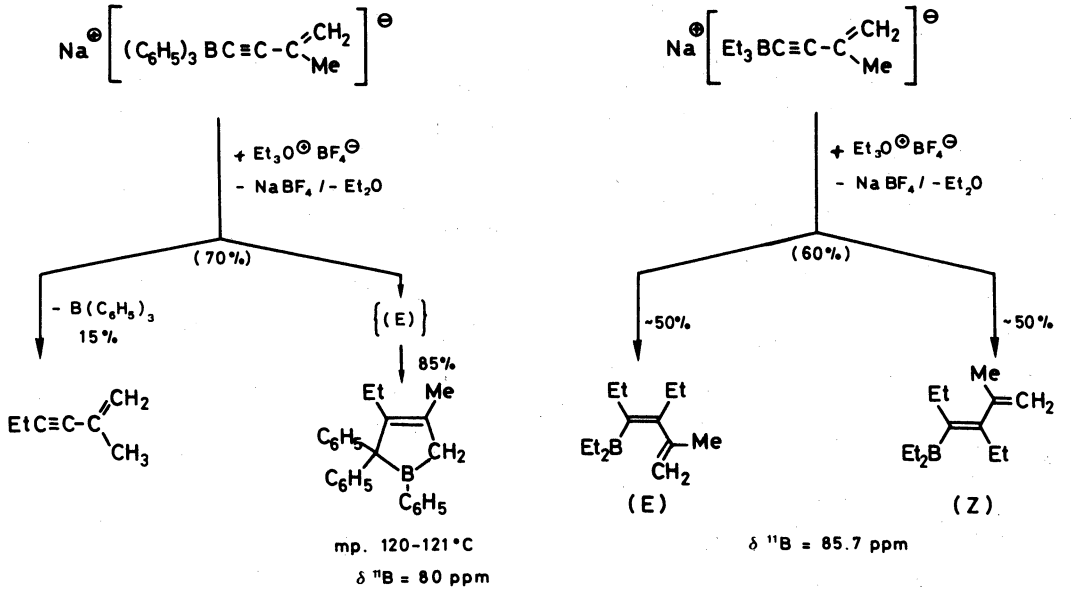

Fig. 8. The influence of B-phenyl- and B-ethylgroups on the formation of tetrasubstituted ethylenes via 1-alkynylborates

ROUTES FOR O-ETHYLBORYLATION

In all the reactions discussed up to now, vinylboranes are obtained in relatively good yields. We then wanted to oxidize these to the synthetically interesting vinyloxyboranes (Ref. 11) using trimethylamine-N-oxide (Ref. 12) in aprotic solvents. This oxidation is sometimes unsuccessful as consecutive reactions occur (Ref. 13).

We were, therefore, forced to look for other ways of preparing dialkylvinyloxyboranes. The main problem was to find an effective O-dialkylborylation agent which reacts under mild conditions with carbonyl compounds. Such an O-dialkylborylating agent is obtained by reaction of an oxy-pyrimidine derivative with a trialkylborane such as triethylborane at 70-80 °C (Ref. 14).

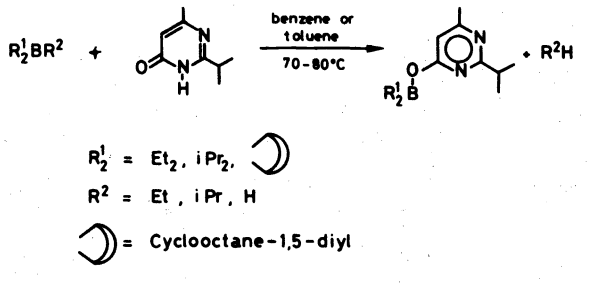

Fig. 9. The preparation of the "low-temperature" borylation reagent

The O-dialkylboryl derivative is able to borylate not only alcohols and amines but also enolizable carbonyl compounds. α-Branched aldehydes react with a stereoselectivity which depends on R^1 and R^2 to give (Z)- and (E)-O-diethylborylaldoenoles. The reaction probably involves a six-centre transition state.

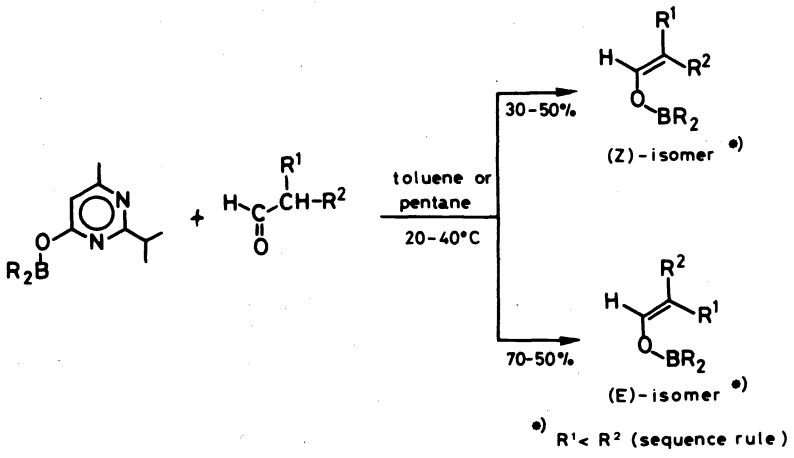

Fig. 10. The (Z/E)-stereoselectivity in the O-borylation of an α-branched aldehyde with the "low-temperature" borylation reagent

An excellent preparative route to O-boryl enoles is afforded by reaction of BEt_3 with ketones in the presence of pivalic acid (Ref. 11). The pure (Z)-isomers can be isolated either directly when the reaction proceeds with high stereoselectivity or after certain (Z/E) separation techniques, when this is necessary (Ref. 11).

2-ETHYL-1,3,2-DIOXA-BORACYCLOALKANES

The addition of the (Z)-isomer of O-diethylborylpropiophenone-enole to propionaldehyde yields the pure erythro O-diethylboryl ketol.

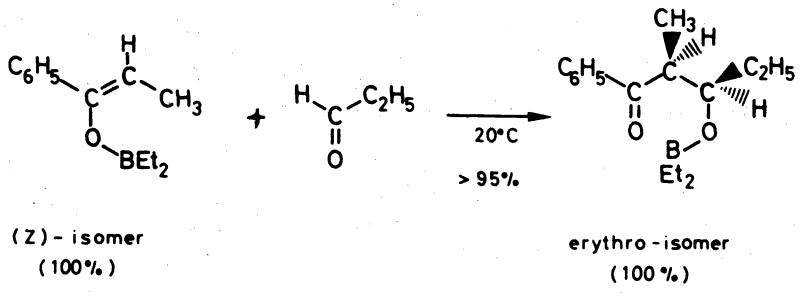

Fig. 11. The stereospecific addition of propionaldehyde to propiophenone O-borylenole (Z-isomer)

The addition which is exo-like has been discussed in greater detail by Dr. Fenzl in his lecture. The erythro forms can be identified by conversion to stereoisomeric 1,3,2-dioxaborinane using a hydroboration/cyclisation reaction.

The ^{1}H-NMR spectra of the latter can then be interpreted as a great deal of information, concerning both position and coupling constants in such heterocycles, has been accumulated in the course of our research.

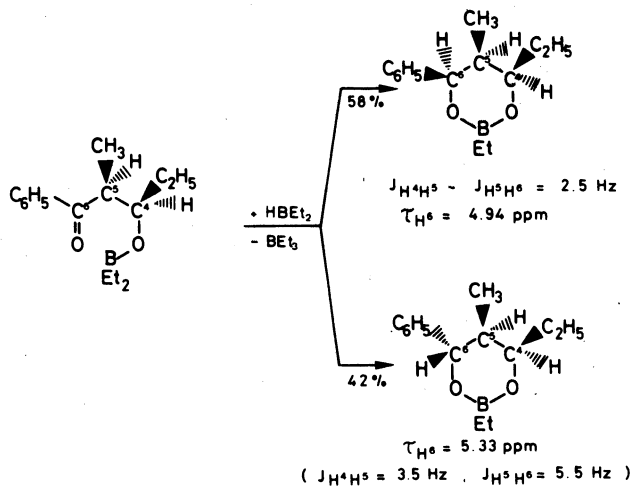

Fig. 12. The formation of isomeric 1,3,2-dioxaborinanes from the erythro isomer

These OBO-rings are formed in a steplike manner. One of these steps is the ligand exchange to give a borane and an ethylboranediyl derivative. This reaction is possible without a catalyst only by heating. One mole of triethylborane can also be eliminated from two O-diethylboryl groups to give the O-ethylboranediyl group by the addition of catalytic amounts of BH-boranes at room temperature.

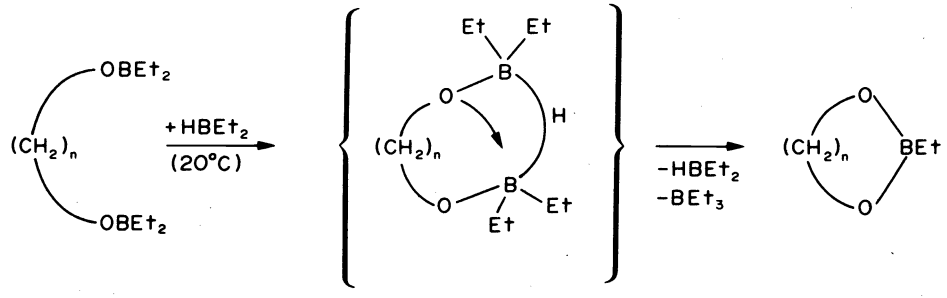

Fig. 13. Ligand exchange in the presence of BH-compounds

Five or six membered rings can be formed. It is often possible to assign structures to different O-ethylboranediyl derivatives with the help of ^{11}B-NMR. The five membered 1,3,2-dioxaborolan-ring has a characteristic resonance signal at δ = +34.5 ppm (relative to the external standard Et_2O-BF_3), whereas the ^{11}B-signal of the six and higher membered OBO-rings lies at δ = +30.5 ppm (Fig. 14).

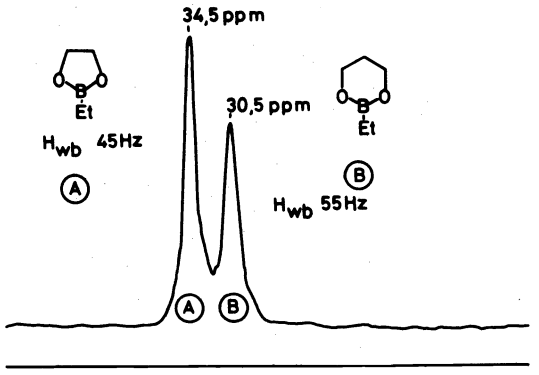

Fig. 14. ^{11}B-NMR-spectrum of an equimolar mixture of borolane and borinane in 2,2-dimethylbutane

O-ETHYLBORONATIONS OF POLYALCOOLS

The next part of this review will deal with some special hydroxy compounds. Some years ago we found that O-dialkylborylation of nearly all hydroxy groups took place with trialkylboranes in the presence of special new catalysts (Ref. 15). The best promotors were R_2BOCOR', mixed anhydrides of a carboxylic acid and a dialkylboryl acid. We also found that the diethylborylation of hydroxy groups could be achieved with the easily obtainable, triethylborane in the presence of small amounts of the liquid, thermally stable diethylborylpivalate $Et_2BOCOtBu$ (Fig. 15).

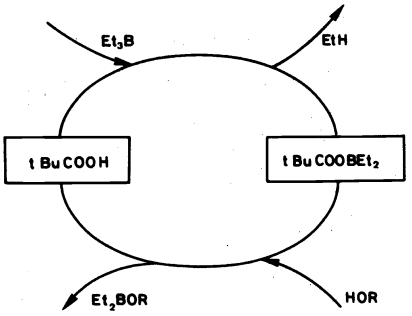

Fig. 15. The catalytic O-diethylborylation cycle

No difficulties are encountered in preparative per-O-diethylborylations. The per-O-diethylboryl derivatives of polyalcohols and saccharides have been prepared in nearly quantitative yield in all cases. The products are usually liquids. The per-O-diethylborylated monosaccharides and hexitols can be vacuum distilled without any decompositions.

Beside the monofunctional O-diethylboryl group, we also have the bifunctional O-ethylboranediyl group. This group can be introduced into hydroxy compounds either directly or indirectly. The indirect method involves the per-O-diethylboryl derivatives as intermediates, from which the O-ethylboranediyl derivatives are obtained in high yields at room temperature in the presence of BH-boranes.

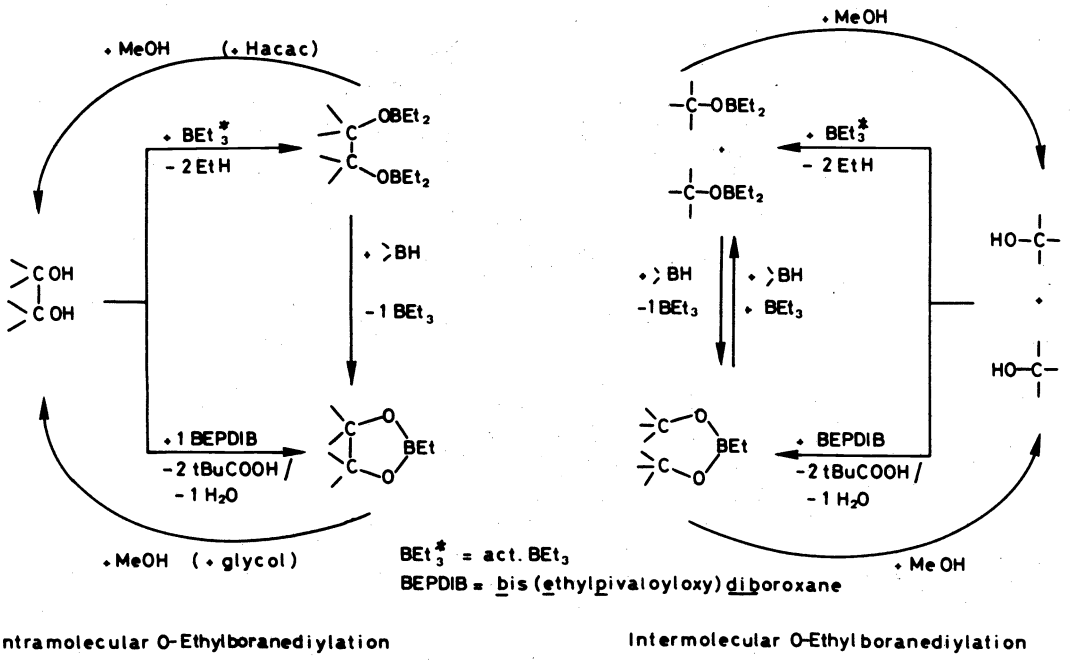

Fig. 16. Formation and transformation of O-ethylboron protective groups

The direct method of O-ethylboranediylation works with two different compounds. The special reagent, bis(ethyl-pivaloyloxy)diboroxane (BEPDIB) reacts at room temperature with hydroxy compounds to give the O-ethylboranediyl derivatives. Water and pivalic acid are formed as side-products. One obtains pure isomer-free anomers from monosaccharides in excellent yields. The O-ethylboranediyl group, formed by reaction with BEPDIB, can link two intra- or two intermolecular hydroxygroups (Fig. 16, Ref. 16). The second reagent for the direct O-ethylboranediylation is triethylboroxine. This compound reacts at about 80 °C with formation of water to O(EtB)-derivatives.

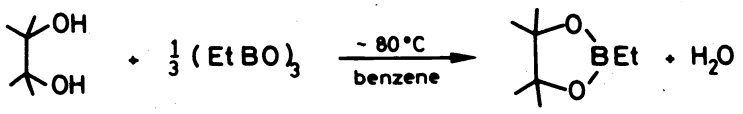

Fig. 17. The O-ethylboranediylation with ethylboroxine

The yields are sometimes lower than with BEPDIB and the purity of the O-ethylboranediyl-products is not always as high. Intermolecular links are not formed so easily with triethylboroxine (Ref. 17).

Each polyhydroxy-compound seems to have its own stable O-ethylboron derivative. In fact, we found that the three hexitols dulcitol (Ref. 18), D-mannitol (Ref. 19) and D-sorbitol (Ref. 17), gave three different O-ethylboranediyl derivatives (Fig. 18).

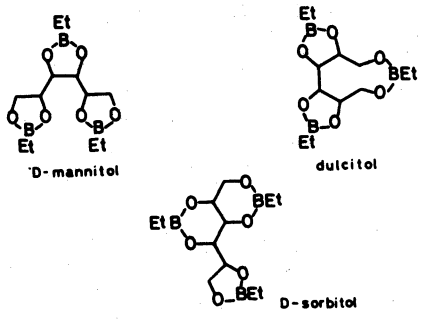

Fig. 18. The three different O-ethylboranediyl derivatives of dulcitol, D-mannitol and D-sorbitol

Pentitols, such as xylitol and ribitol, reacted with BEPDIB, or via the per-O-diethylboryl compounds, to give derivatives containing two O-ethylboranediyl rings. The bis-1,2:3,5-O-ethylboranediyl-4-diethylborylxylitol was obtained nearly quantitatively from xylitol via the three independent indirect routes. With BEPDIB in excess, by the direct route, one obtains a compound with an intermolecular O-alkylboranediyl group.

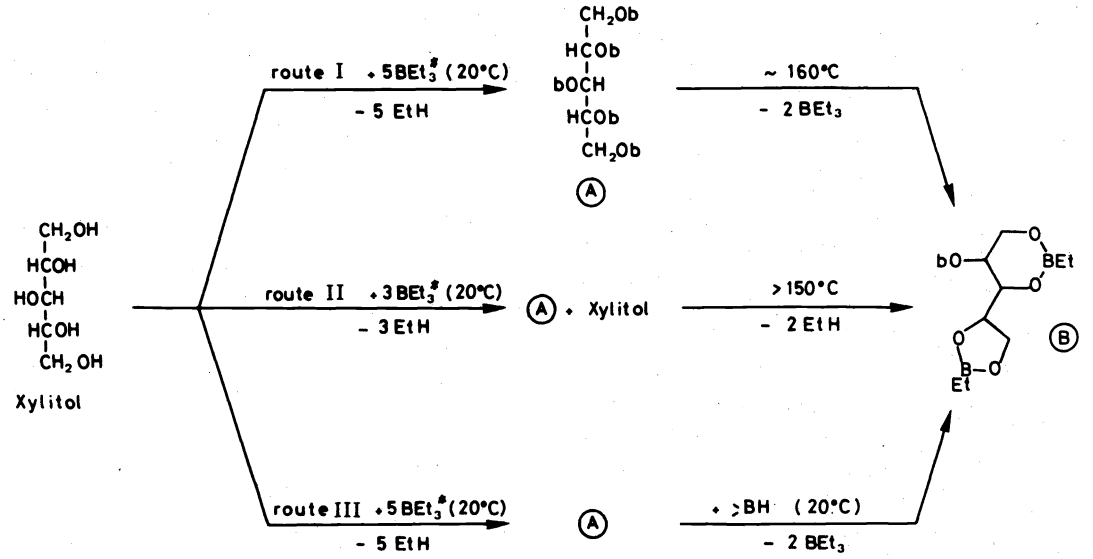

Fig. 19. Preparation of 1,2:3,5-bis-O-ethylboranediyl-4-O-diethylborylxylitol

The O-acetylation of xylitol via the ethylboron derivatives is shown in Fig. 20. It is possible to obtain 1,2,3-tris-O-acetylxylitol in high yield (Ref. 16).

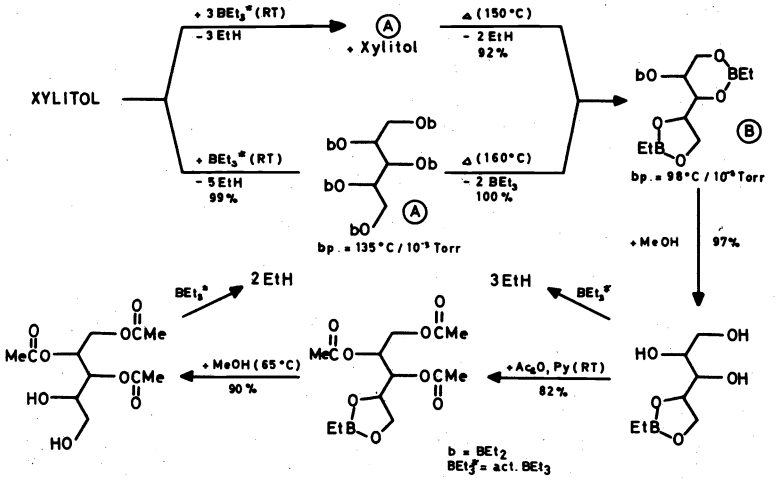

Fig. 20. O-Acetylation of xylitol via O-ethylboron derivatives

O-ETHYLBORON DERIVATIVES OF MONOSACCHARIDES

Figs. 21 and 22 show the selective O-acylation of D-glucose (Ref. 16) and of D-fructose (Ref. 17).

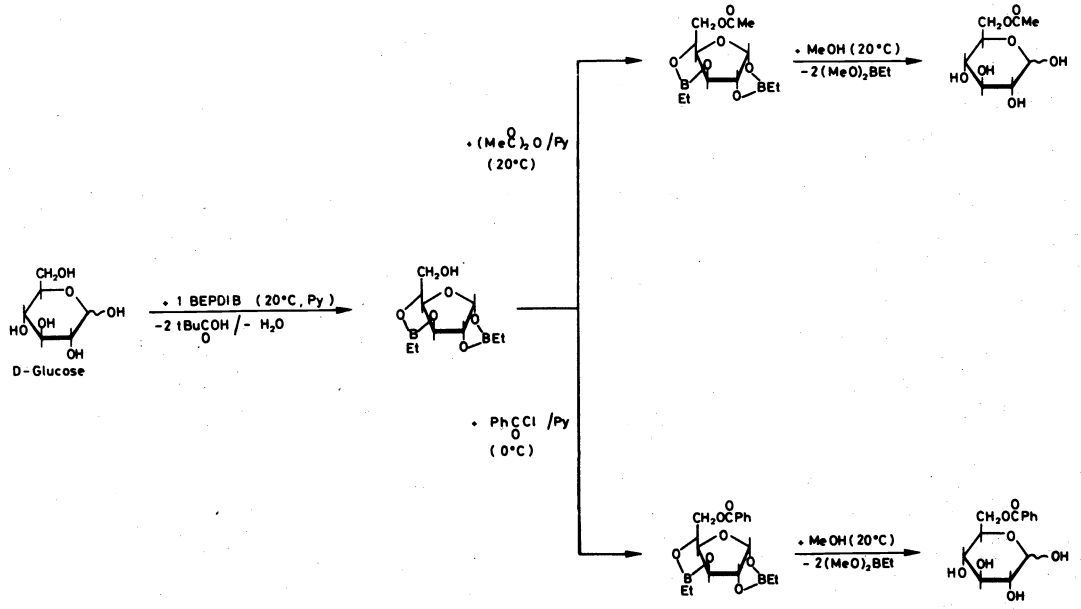

Fig. 21. Preparation of 6-O-acyl-D-glucopyranoses via O-ethylboranediylglucofuranose

Pure bis-O-ethylboranediyl derivatives which contain one free hydroxy group are obtained on reaction of these two sugars with one mole of BEPDIB. The ^{1}H-NMR spectrum of 2,3:4,5-bis-O-ethylboranediyl-ß-D-fructopyranose is shown in Fig. 23. Only one isomer is formed.

The ^{1}H-NMR spectra of the various O-ethylboranediyl derivatives of polyols are simpler than those of the per-O-diethylboryl derivatives. The former compounds have structures with fixed conformations at room temperature.

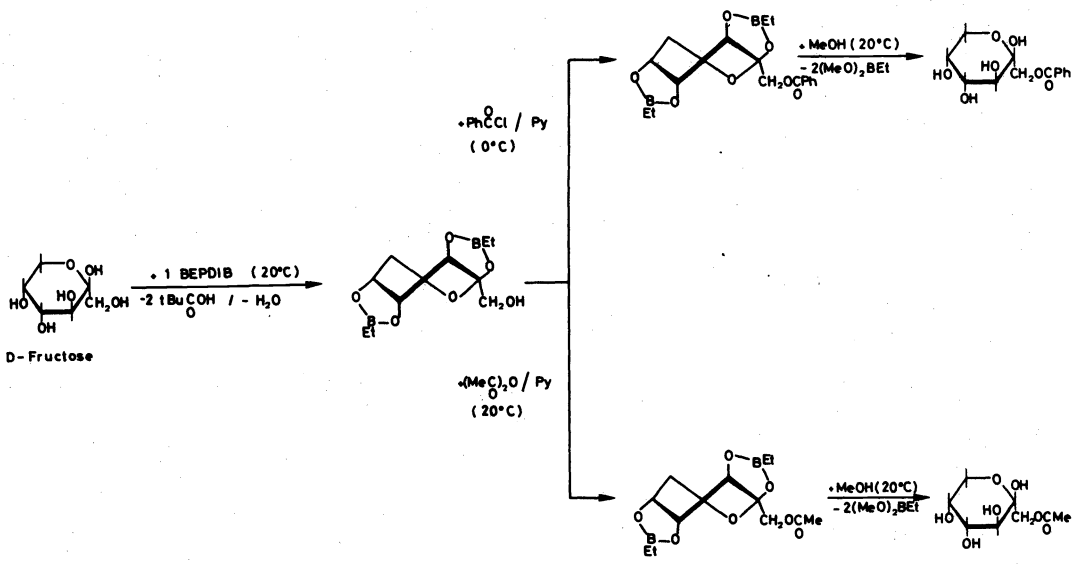

Fig. 22. Preparation of 1-O-acyl-D-fructopyranoses using the O-ethylboranediyl protective group

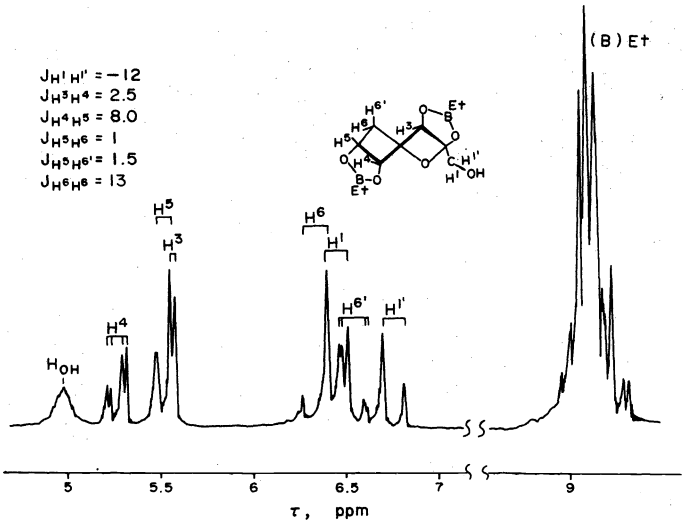

Fig. 23. ^{1}H-NMR-spectrum (100 MHz, d_6-DMSO) of 2,3:4,5-bis-O-ethylboranediyl-ß-D-fructopyranose

The reactions of 6-deoxy-L-mannose (L-rhamnose) with ethylboron compounds are rather complicated and somewhat surprising. A simplified scheme (Fig. 24) shows, that the reaction with one mole of BEPDIB, at room temperature, yielded the vacuum distillable, pure bis-1,2:3,5-O-ethylboranediylfuranose derivative (Ref. 16).

The selective deborylation of this bis-O-ethylboranediyl derivative with methanol, at room temperature, did not yield mono-1,2-O-ethylboranediyl- or a mono-3,5-O-ethylboranediyl-L-rhamnofuranose. Instead 2,3-O-ethylboranediyl-L-rhamnofuranose was formed by an intramolecular transesterification. This compound could not be vacuum distilled. A disproportionation occured at the temperature required for distillation yielding L-rhamnose and its bis-1,2:3,5-O-ethylboranediyl derivative. The 2,3-O-ethylboranediyl derivative could be O-acetylated in good yield. After the total deborylation with ethylene glycol one obtains 1,5-di-O-acetyl-L-rhamnofuranose, which could not be prepared via the O-isopropylidene intermediates.

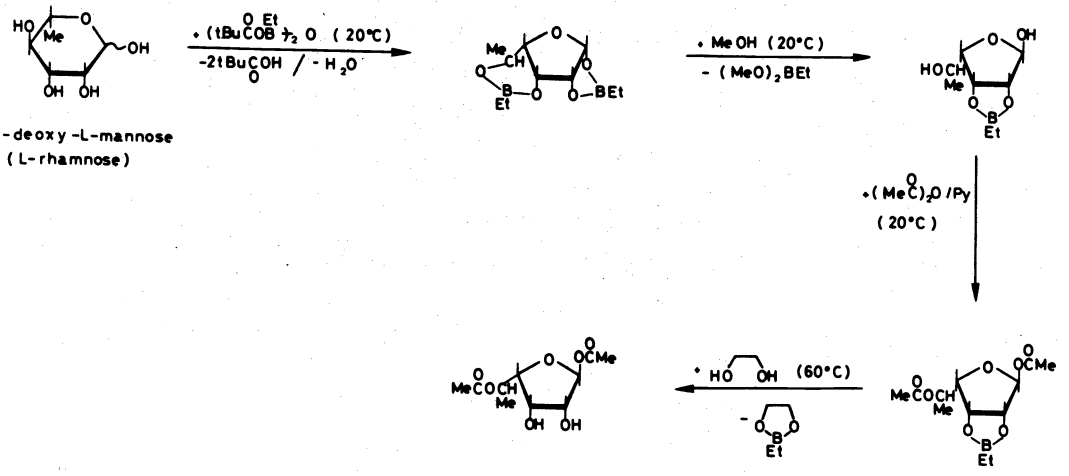

Fig. 24. 1,5-Di-O-acetyl-6-deoxy-α-L-mannofuranose (L-rhamnose) via O-ethylboranediyl intermediates

CONDENSATIONS OF CARBONYL COMPOUNDS

BEPDIB can be prepared by reaction of diethylborylpivalate with water (Fig. 25). This compound is, in effect, an excellent dehydrating agent for the condensation of various carbonyl compounds (Ref. 20). Two moles of this reagent react with 1 mole water with liberation of 2 moles ethane to give the solid bis(ethyl-pivaloyloxy)diboroxane (=BEPDIB) (Ref. 21), which is easily separated from the product mixture.

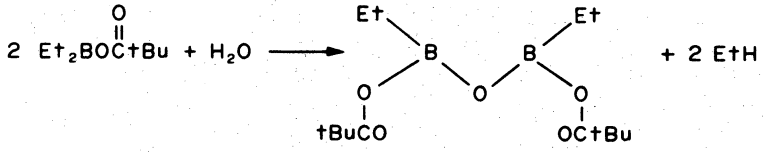

Fig. 25. The reaction of diethylborylpivalate with water to BEPDIB

Compared with the common classical condensation agents in protonic solvent, the diethylborylpivalate condensation usually gives purer products in higher yields. Fig. 26 shows some mixed condensation products of ketones, which are formed via ethylboron intermediates (Ref. 22).

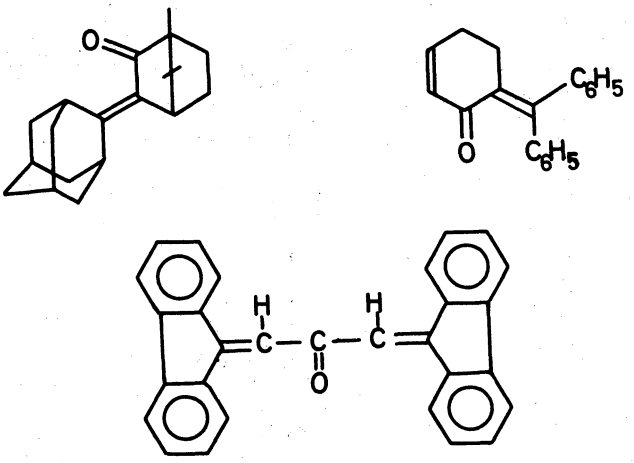

Fig. 26. Some condensation products of ketones with diethylborylpivalate

Homocondensations of ketones and of aldehydes are also possible with the same reagent at 100-120 °C. Above 150 °C the aldol addition or condensation products react with diethylborylpivalate yielding organoboranes. New BC-bonds are formed by the elimination of pivalic acid (Ref. 22). Several examples of these BO-heterocycles are shown in Fig. 27.

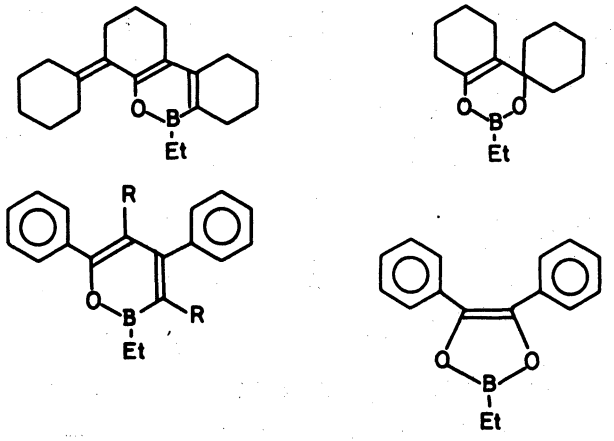

Fig. 27. Some BO-heterocycles from ketone condensates and BEPDIB

QUANTITATIVE DETERMINATIONS OF HYDROXY-GROUPS

The activated hydrolysis of triethylborane in the presence of pivalic acid is well suited for the quantitative determination of water in salt hydrates (Fig. 28, Ref. 23). Other gas-volumetric methods do not give acceptable results.

salt hydrate	cat.[b]	t_{max} [°C]	time[c] [min.]	obs. H_2O $\left[\frac{obs.}{calc.} \times 10^2\right]$ cat: -	cat: +
$Li_2SO_4 \cdot H_2O$	-	100	20	84.2	
	+	60	10		97.2
$Na_2S \cdot 9\ H_2O$	-	95	20	17.2	
	+	35	4		96.4
$Na_2S_2O_3 \cdot 5\ H_2O$	-	15	10	92.6	
	+	35	10		101.1
$Na_3PO_4 \cdot 12\ H_2O$	-	100	20	13.22	
	+	50	3		101.1
$Na_4P_2O_4 \cdot 10\ H_2O$	-	70	10	93	
	+	35	5		98.3
$Na_2Cr_2O_7 \cdot 2\ H_2O$	-	50	20	101.7	
	+	50	10		100.8
$NaVO_3 \cdot 4\ H_2O$	-	60	10	65.6	
	+	45	1		104.8
$CaCl_2 \cdot 4\ H_2O$	-	60	10	73.5	
	+	50	10		100.9
$Ca(NO_3)_2 \cdot 4\ H_2O$	-	55	20	90.4	
	+	50	5		102.9
$MnCl_2 \cdot 4\ H_2O$	-	60	10	90	
	+	60	5		102.4
$FeCl_2 \cdot 4\ H_2O$	-	100	20	94.6	
	+	50	10		100

a) Volumetric determination of the evolved ethane
b) with catalyst (diethylborylpivalate): +
without catalyst: -
c) time for gas evolution (r. t. to t_{max})

Fig. 28. Quantitative water determination in salt hydrates with activated triethylborane

The reactions with triethylborane, on the other hand, are fast and occur to completion at 50-60 °C. Two examples are given in Fig. 29 for the preparation of anhydrous $FeCl_2$ and SrO.

$$2\ Et_3B + H_2O \xrightarrow[20°C]{cat.^{x)}} 2\ EtH + (Et_2B)_2O$$

$$FeCl_2 \cdot 4\ H_2O + 8\ BEt_3 \xrightarrow[<60°C]{cat.^{x)}} 8\ EtH + FeCl_2 + 4(Et_2B)_2O$$

$$Sr(OH)_2 \cdot 8\ H_2O + 18\ BEt_3 \xrightarrow[\sim 50°C]{cat.^{x)}} 18\ EtH + SrO + 9(Et_2B)_2O$$

$^{x)}$ cat. = diethylborylpivalate

Fig. 29. The quantitative dehydration of salts with activated triethylborane

Both, ethyl- and propyldiborane, which react quickly with unbound water at room temperature, react a lot slower than activated triethylborane with salt hydrates. A further disadvantage of alkyl diboranes is, that many metals salts are easily reduced by the BH boranes (Ref. 23).

The difference between activated triethylborane and ethyl- or propyldiboranes is even more noticable in reactions with the hydroxyl groups of polyhydroxy compounds. All the hydroxy groups in mono-, di-, oligo- and polysaccharides react quickly at ca. 50 °C with the first ethyl group of triethylborane ; but e.g. cellulose is absolutely inert to propyldiborane at 130 °C; no gas is evolved (Ref. 15).

These differences in reactivity reflect two different mechanisms in the protolyses. In the case of activated triethylborane a two stage catalytic cycle is involved. The BH-protolysis, however, must involve the electrophilic addition of the borane to an O-atom, which then requires a further hydroxyl group in its proximity in order to react. Whereas the lower molecular weight polyalcohols allow such an interaction due to the conformational flexibility, the higher molecular compounds have a fixed conformation which hinders reaction.- The hydroxy group determination using activated triethylborane is, however, not successful in all cases e.g. the carboxyl group of potassium phthalate does not react. The acidic hydrogens can however be determined quantitatively by addition of chlorodipropylborane (Ref. 23). Similarly, reaction of sodium bicarbonate results in evolution of ethane and 1 mole carbon dioxide.

Compound	cat.[b]	t_{max} [°C]	time[c] [min.]	obs. H_2O $\left[\frac{obs.}{calc.} \times 10^{-2}\right]$ cat.: -	+
D(+)-Xylose	-	60	15	102	
	+	20	1		101
L(+)-Arabinose	-	30	10	99.2	
	+	30	1		101
D(+)-Glucose	-	70	30	98.9	
	+	25	1		99
D(-)-Fructose	-	60	15	101	
	+	40	2		101
Maltose	-	70	25	102	
	+	25	1		106
Raffinose-Hydrate	-	70	20	100.5	
	+	30	5		99
Cellulose	+	60	80		101
4,6-O-Benzylidene-D-glucopyranose	-	80	30	98	
	+	25	5		102
L(+)-Ascorbic acid	-	80	120	101	
	+	30	60		98
Methyl 3-deoxy-3-amino-ß-D-glucopyranoside	-	80	120	82	
	+	25	7		101

a) Volumetric determination of evolved ethane
b) with catalyst (diethylborylpivalate): +
without catalyst: -
c) time for gas evolution (r. t. to t_{max})

Fig. 30. Quantitative determination of OH-groups with activated triethylborane

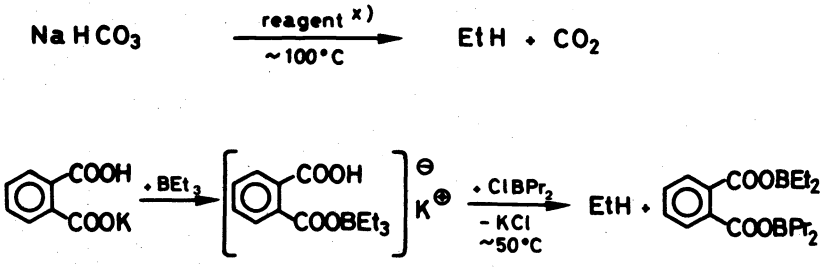

Fig. 31. Determination of acidic hydrogens with $BEt_3/ClBPr_2$

SEPARATIONS OF SACCHARIDES

Finally, I would like to return to the sugar boronation and give some examples of separations that were carried out with the help of the O-ethylboronation/deboronation procedures. Many saccharides can be purified via ethylboron intermediates (Ref. 16).

The volatile O-ethylboron derivatives of monosaccharides can easily be separated from di- and higher saccharides. Thus, after reacting a mixture of glucose and sucrose with activated triethylborane, the pentakis-O-diethylborylglucose can be distilled off from the per-O-diethylborylated disaccharide. Treatment of distillate and residue with methanol affords pure glucose and sucrose (Ref. 16), respectively.

The special property of the O-ethylboranediyl group to form intra- and intermolecular products can be used for the separation of polyhydroxy compounds.

When one mole of the aldohexoses D-glucose, D-mannose and D-galactose was allowed to react with one mole BEPDIB at room temperature vacuum distillable bis-O-ethylboranediyl derivatives were obtained (Fig. 32). The D-mannose derivative had a furanose ring and the D-galactose derivative a pyranose ring. Both structures were analogous to the O-isopropylidene derivatives. The D-glucose derivative, on the other hand, forms an unusual 1,2:3,5-furanose ring system. The free hydroxy groups in each of the above mentioned bis-boron derivatives reacted with an excess of BEPDIB at room temperature to form non-distillable intermolecular O-ethylboranediyl products. The structures of these products are shown in Fig. 32. The properties of these intermolecular derivatives may be used for separation purposes (Ref. 16).

Thus, xylitol and D-mannitol can be converted to their respective O-ethylboranediyl compounds with BEPDIB or via the per-O-diethylboryl derivatization with BH-catalysts (Fig. 33, Ref. 16).

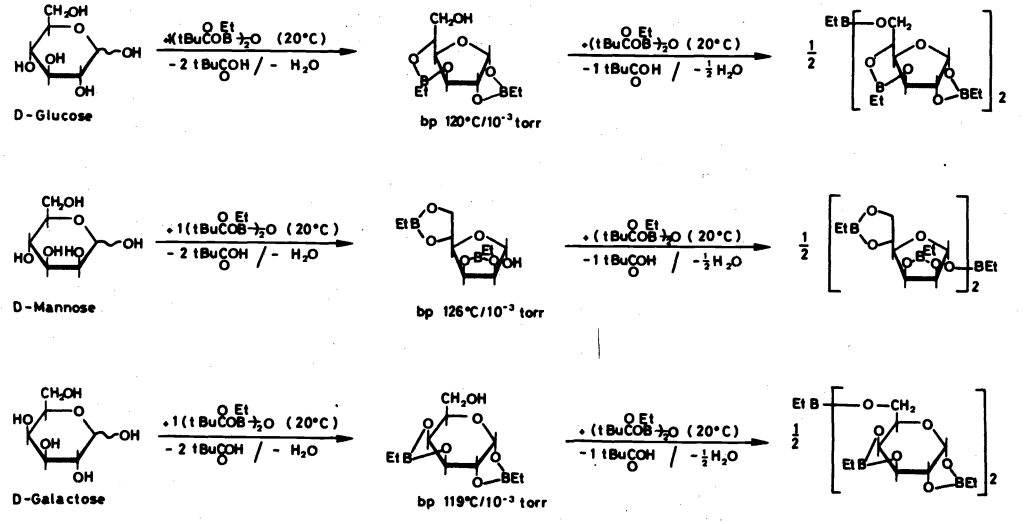

Fig. 32. Intra- and intermolecular O-ethylboranediylation of some hexoses

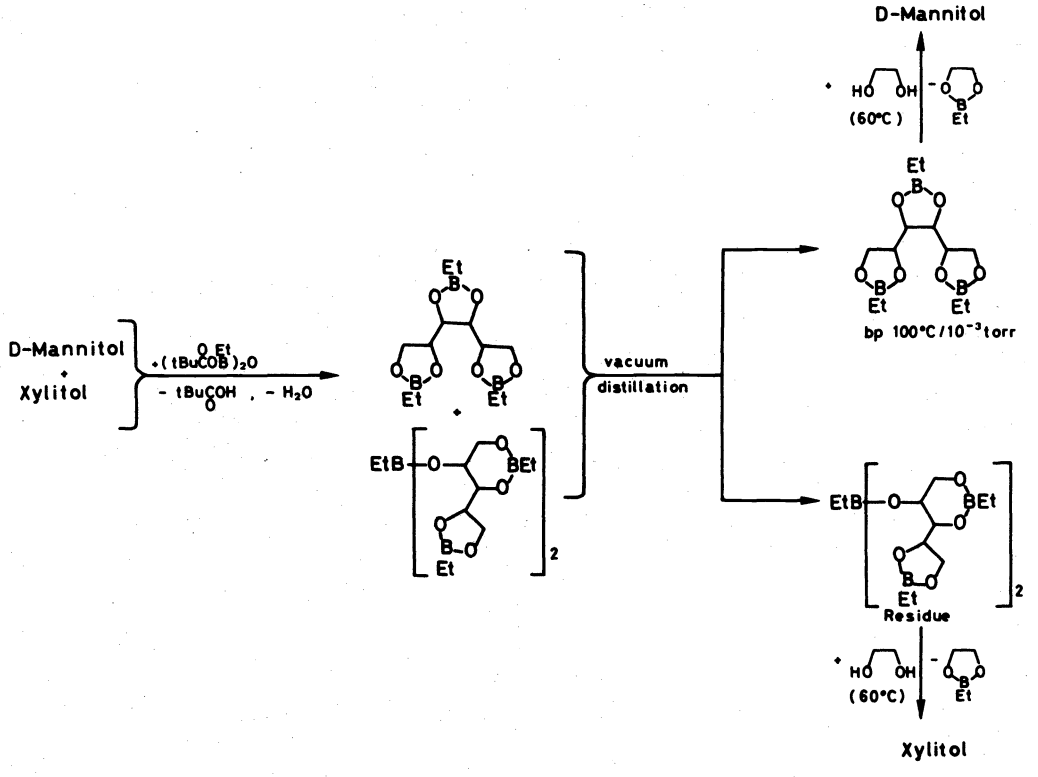

Fig. 33. The separation of a D-mannitol/xylitol mixture via O-ethylboranediyl intermediates

Intra- and intermolecular reactions with triethylborane occur with xylitol, whereas D-mannitol forms intramolecular O-ethylboranediyl groups only. The mannitol derivative can therefore be distilled off quantitatively from the mixture and the xylitol "dimer", remains as a residue. Pure D-mannitol and xylitol can then be regenerated by deboronation with ethylene glycol (Ref. 16).

The same separation method can be carried out with a mixture of L-arabinose and D-mannose. With an excess of BEPDIB at room temperature one obtains the O-ethylboranediyl derivatives. The bis-O-ethylboranediyl-L-arabinose can be distilled off and yields pure L-arabinose on methanolysis. Pure D-mannose can also be regenerated from the distillation residue by treatment with ethylene glycol (Ref. 16).

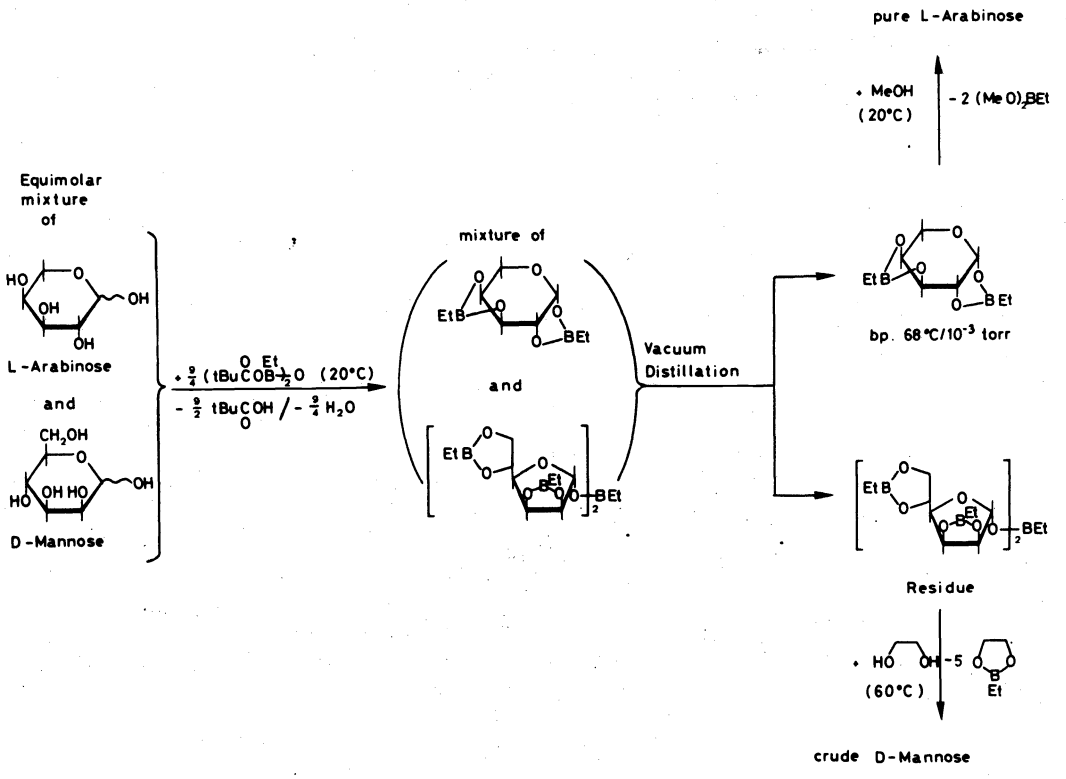

Fig. 34. The separation of L-arabinose and D-mannose via EtB-intermediates

D-xylose and xylitol can also be easily separated using the O-ethylboranediylisation/deboronation procedure. A mixture formed in the reduction of xylose can be reacted with either a) excess BEPDIB in pyridine at 20 °C or b) with excess ethylboroxine in benzene at 80 °C to yield products which are conveniently separated by distillation. On deborylation of the distillate with methanol pure D-xylose is obtained. The residue after distillation can be treated with triethylborane containing catalytic amounts of BH to give a distillable boronated xylitol, which on total deboronation with ethylene glycol gives pure xylitol (Ref. 17).

One application of the borylation/deborylation procedure is the preparation of pure amylose. It was possible to separate the high molecular linear amylose part of native starch from the branched amylopectin part by using the simple borylation/deborylation method (Fig. 36). Anhydrous corn starch was O-diethylborylated with activated triethylborane in hexane at room temperature. The insoluble component, composed of nonborylated amylopectin, was filtered off and the soluble portion, consisting of per-O-diethylborylated amylose, was treated with methanol to give a pure amylose (Ref. 15 and 16).

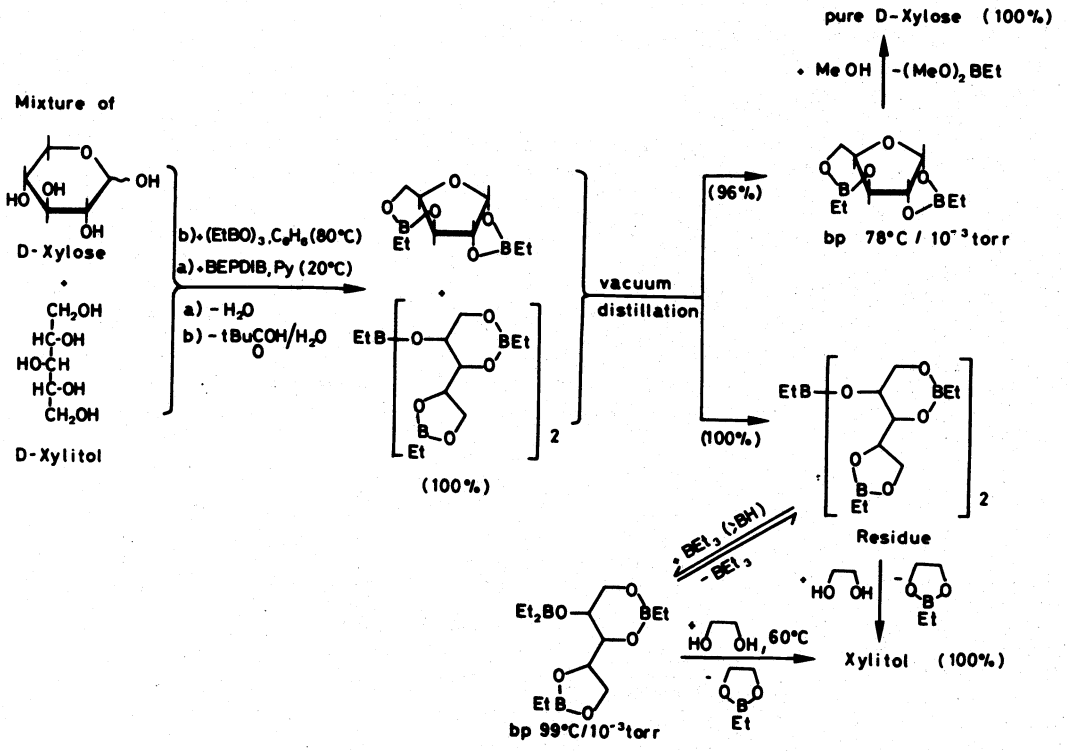

Fig. 35. The separation of a D-xylose/xylitol mixture via O-ethylboranediyl-intermediates

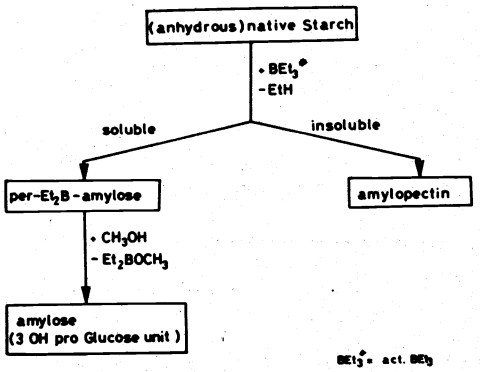

Fig. 36. Separation of amylose and amylopectin via the borylation/deborylation procedure

I hope, that the few examples in synthesis and analysis have shown the broad and specific applications of organoboranes. These simple compounds can sometimes be a great help in improving known syntheses of organic compounds. Sometimes they open up new or better ways to certain derivatives. The advantages of some organoboranes in chemical analysis are a further reason for investigating the properties of these compounds.

Finally, I would like to thank all the people whose excellent contributions I dealt with in the different parts of my talk. The syntheses via 1-alkynylborates were investigated by Dr. P. Binger, Dr. L. Hagelee and by G. Seidel. The stereochemistry of the vinyloxyboranes was studied by Dr. W. Fenzl. The new ways to the boronated hydroxy compounds were investigated by Dr. W. V. Dahlhoff. Last but not least the analytical methods were accurately carried out by W. Schüßler. We think that organoboranes will have a great future in synthesis and analysis.

REFERENCES

1. P. Binger and R. Köster, Tetrahedron Letters 1965, 1901.
2. A. Pelter, C.R. Harrison and D. Kirkpatrick, J. Chem. Soc. Chem. Commun. 1973, 544.
3. P. Binger, Angew. Chem. internat. Edit. 6, 84 (1967).
4. P. Binger, Tetrahedron Letters 1966, 2675.
5. P. Binger and R. Köster, Synthesis 1973, 309.
6. P. Binger and R. Köster, J. Organomet. Chem. 73, 205 (1974).
7. P. Binger and R. Köster, Synthesis 1974, 350.
8. P. Binger and R. Köster, Chem. Ber. 108, 395 (1975).
9. R. Köster and L. Hagelee, Synthesis 1976, 118.
10. R. Köster and G. Seidel, unpublished results.
11. W. Fenzl and R. Köster, Liebigs Ann. Chem. 1975, 1322; see leading references therein.
12. R. Köster and Y. Morita, Liebigs Ann. Chem. 704, 70 (1967).
13. R. Köster and K.-L. Amen, unpublished results, K.-L. Amen, Dissertation Universität Bochum 1970.
14. W. Fenzl, H. Kosfeld and R. Köster, Liebigs Ann. Chem. 1976, in press.
15. R. Köster, K.-L. Amen and W.V. Dahlhoff, Liebigs Ann. Chem. 1975, 752.
16. R. Köster and W.V. Dahlhoff, ACS-Meeting April 1976, New York.
17. W.V. Dahlhoff and R. Köster, unpublished results.
18. W.V. Dahlhoff and R. Köster, J. Org. Chem. 98, in press (1976).
19. W.V. Dahlhoff, W. Schüßler and R. Köster, Liebigs Ann. Chem. 1976, 387.
20. R. Köster and A.-A. Pourzal, Synthesis 1973, 674.
21. R. Köster, H. Bellut and W. Fenzl, Liebigs Ann. Chem. 1974, 54.
22. A.-A. Pourzal, Dissertation Universität Bochum 1974.
23. R. Köster and W. Fenzl, Liebigs Ann. Chem. 1974, 69.