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Allylic boranes are chemist's best friends: Reactivity, applications, new opportunities

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ABSTRACT

Fruitful methods for the preparation of various (poly)unsaturated, (poly)cyclic and cage organic compounds with the use of allylic type organoboranes have been developed. Allylborane reactions proceeding with the rearrangement of allylic moiety or via a direct rupture of the B–C bond (with retention) little known to the boron community are considered. Synthesis of boron containing clathrochelates and some transformations of 1-boraadamantane, a unique cage compound, are also described.

1. Introduction

For decades, β,γ-unsaturated (allylic) boron compounds have been employed in organic synthesis due to their high reactivity, great variety reactions, high yields of the products and an excellent enantioselectivity of the allylboration of aldehydes and aldimines with chiral allylboranes [1–5] as well as the unique dynamic behaviour (borotropy [1,3], boron shifts) [6,7]. Various relatively simple and complicated natural compounds are available now through the use of allylic boranes.

For the chemists, the words "allylic boranes" mean a class of reactive compounds on which basis a clever brain and skilful hands can make everything.

A great diversity of allylic type boranes and boronates (more than 100) have been prepared [5]. Selected systems we are working with are presented in Scheme 1 while the most important chiral allylating reagents are shown in Scheme 2 [5].

Over 40 various allylborane reactions are now known and all were generalized and divided into six types depending on the center at which the reaction takes place. In fact, allylborane molecules contain five reaction centers: the boron atom, B–C, C=C, C_α–H and B–X bonds, while the peculiarities of these compounds are manifested in the reactions involving the allylboron system as a hole (Fig. 1). All these reactions have been considered in the review [5].

The B–C bond in triallylborane (1.580(2) Å, gas electronography) [8] is longer than in triethylborane (1.573(2) Å) [9]. The energy of the B–C(allylic) bond was estimated to be *ca* 68 kcal/mol [10] which is lower in comparison with 82–87 kcal/mol for trialkylborane [11]. Complexation with bases ($R_3B \leftarrow L$) which is the first stage of the most organoborane reactions (e.g. with the C=O, C=N, C≡C bond) leads to the elongation of the B–C bond(s) (≥1.62 Å) [9,12] and consequently to its (their) weakness.

In this paper, four allylborane reactions (of seven studied) proceeding with direct rupture of the B–C bond as well as certain mono-, di- and triallylboration reactions, little known to the boron community, are discussed. In addition, synthesis of boron containing clathrochelates and some transformations of 1-boraadamantane, a unique cage compound, are also described. It should be mentioned that triallylborane and 1-boraadamantane are isomers ($C_9H_{15}B$).

2. Reactions with the B–C bond direct cleavage

These reactions are common to allyl- and alkylboranes and proceed with retention of configuration.

2.1. Reactions with bicyclo[1.1.0]butane and [1.1.1]propellane

These hydrocarbons are highly strained substances (Fig. 2).

Cyclopropane tolerates heating with triallylborane up to 100 °C while reactions of bicyclo[1.1.0] butane with triallyl- and

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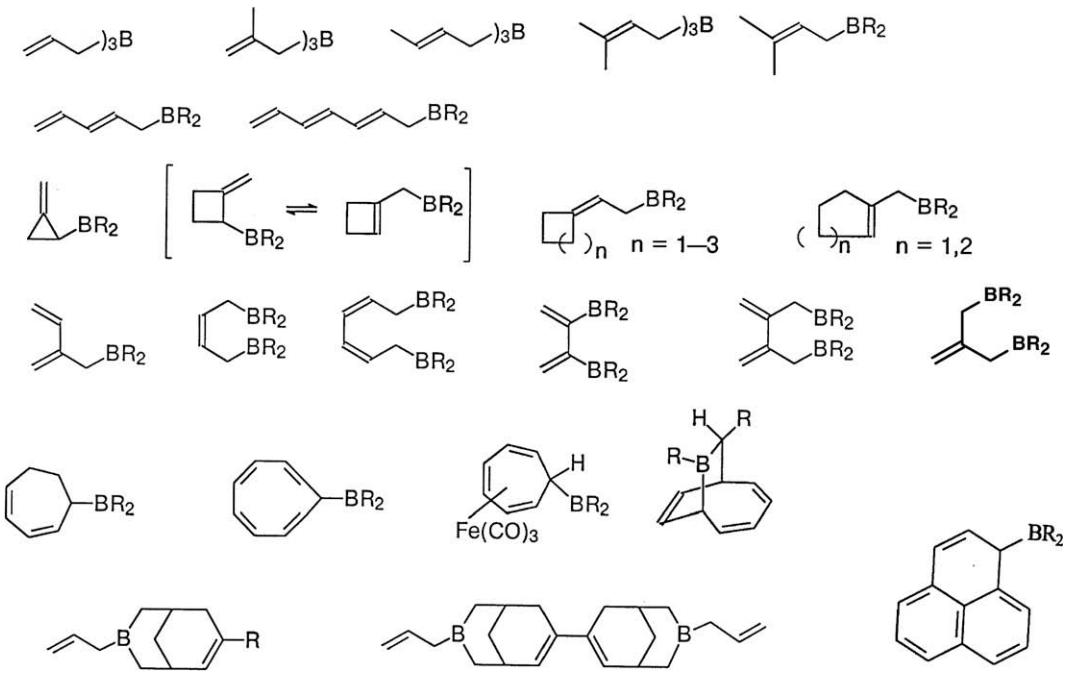
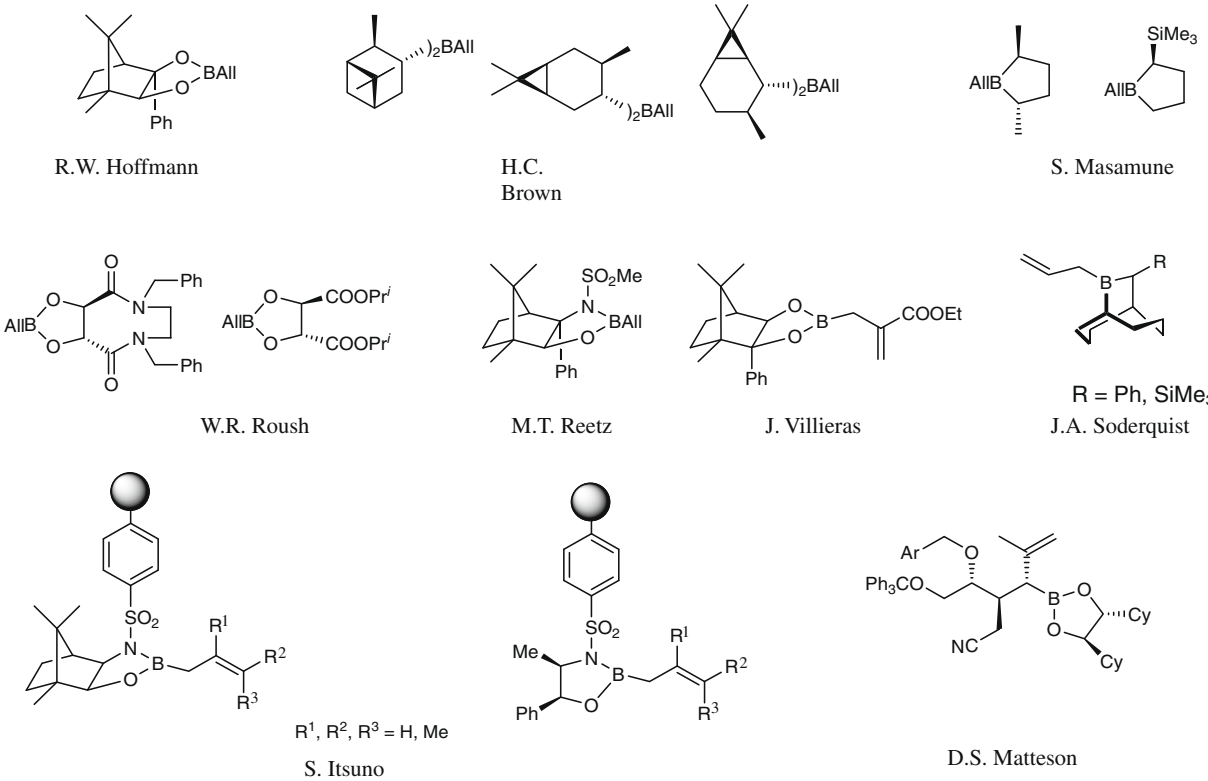


Scheme 1.



Scheme 2.

tripropylboranes proceed exothermically under mild conditions to give the secondary butenyl boranes **1** which were oxidized to the corresponding alcohols **2** (Scheme 3) [13]. When tricrotylborane ($E{:}Z \approx 7{:}3$) was used, a 7:3 mixture of *E*- and *Z*-diene carbinols **3a** and **3b** was obtained; this result shows cleanly that R group migration occurs with retention of configuration.

Plausible mechanism of the reactions is shown in Scheme 4.

The first step seems to be a complexation of R_3B with bicyclo[1.1.0]butane molecule **4**. Then the central bond is cleaved

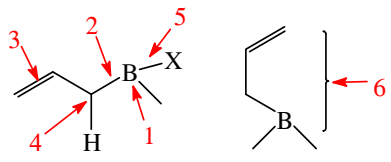


Fig. 1. Allylic borane reaction centres.

and the betaine **5** is formed. The latter is transformed into the intermediate **6** which rearranges to the final product via migration of R^- from the negatively charged boron to the neighbouring carbon with positive charge.

It is not unlikely the reaction occurs as one act (**7**).

[1.1.1]Propellane system is also cleaved under the action of triallyl- and trialkylboranes to produce two products, mono-**11** and bis-cyclobutane **12** derivatives (Scheme 5) [14]. The reactions are also highly exothermic.

When triallylborane and propellane were utilized in a ratio 1.5:1, the major product was the bicyclic derivative (**12**, >58%). The latter is formed (>22%) even with high excess of triallylborane (6:1). These results can be explained by the higher reactivity of the B–C(cyclobutyl) bond (in **11**) in the reaction in comparison with the reactivity of the B–C bonds in starting symmetrical triorganoboranes.

We believe that a cleavage of the central C–C bond of [1.1.1]propellane with R_3B is the first step of the reaction. The betaine **9** thus formed is unstable and transformed to the new betaine **10** through the rupture of the bicyclic C–C bond. The final stage is the anionotropic 1,2-shift of the alkyl (allyl or cyclobutyl) group from the boron atom to α-carbon bearing positive charge (**10**). Cyclobutane alcohols **13** and **14** were prepared through oxidation of boranes **11** and **12**.

2.2. Reactions with ethyl orthoformate

Thermal reaction (140 °C) of triallylborane with ethyl orthoformate gave rise to diethyl triallylmethylboronate **15**, ethyl diallylborinate and propene [15]. Trialkylboranes react similarly forming the corresponding ethyl dialkylborinates and trialkylmethylboronates **16**. Triallyl- and trialkylmethanols were prepared by the following oxidation of the boronates (Scheme 6).

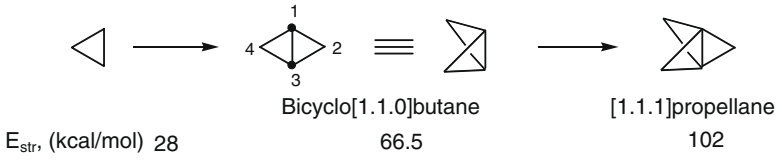
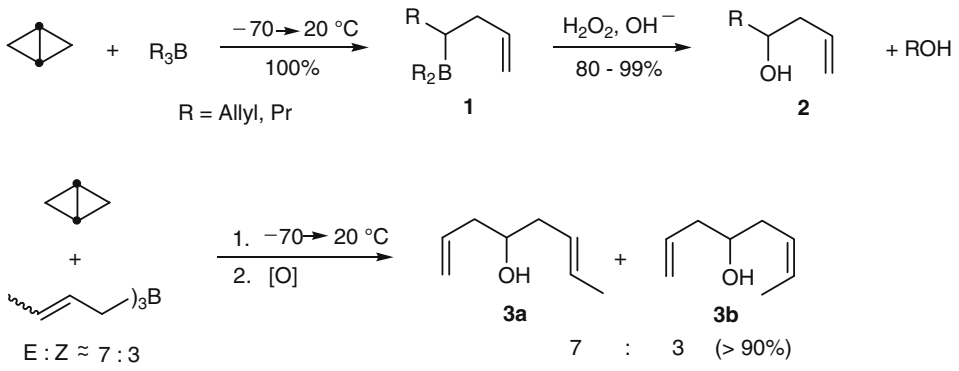
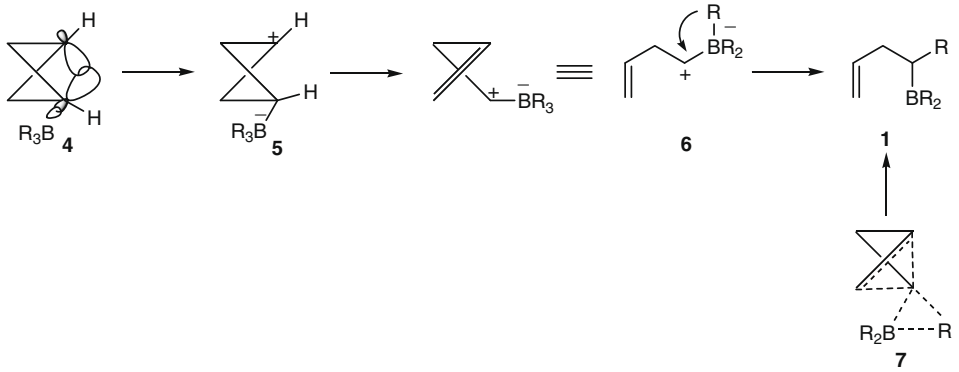


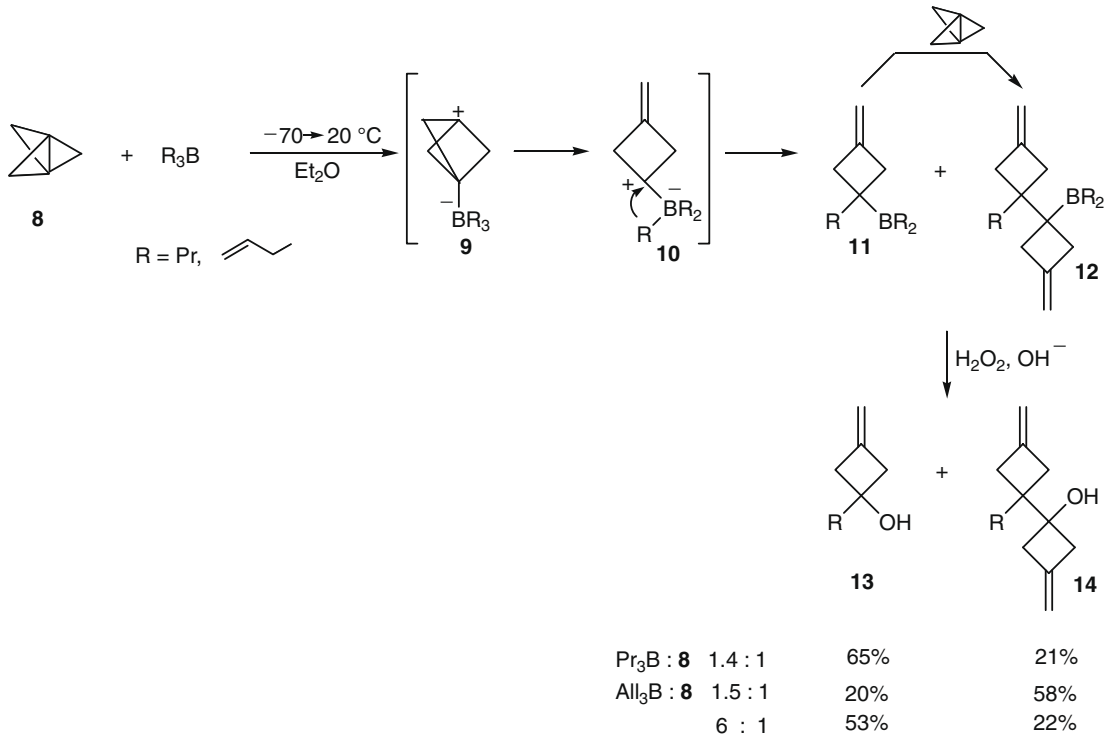
Fig. 2. Strain energy (E_{str}) of cyclopropane derivatives.



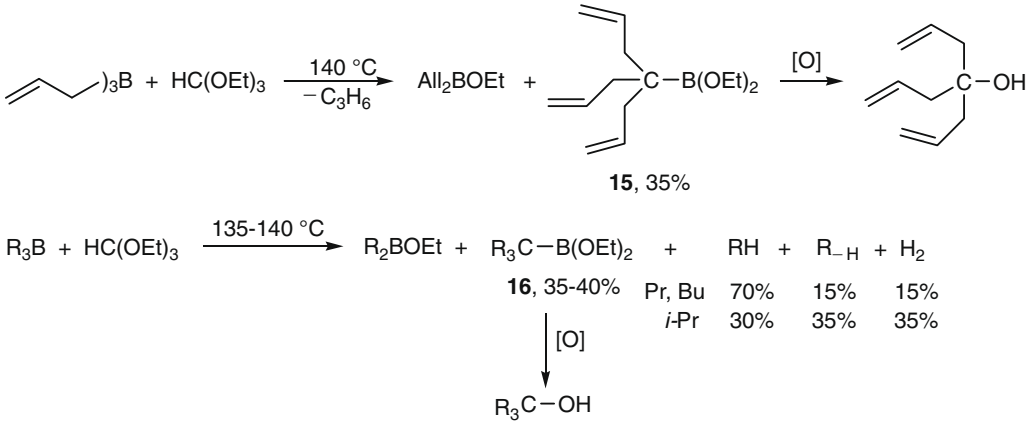
Scheme 3.



Scheme 4.



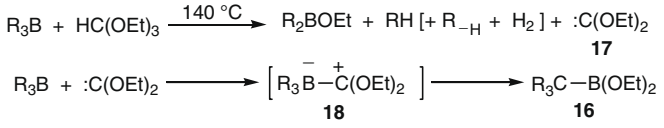
Scheme 5.



Scheme 6.

In general, this reaction presents a convenient way to tertial alcohols if (!) the corresponding RR^1R^2B is not so expensive.

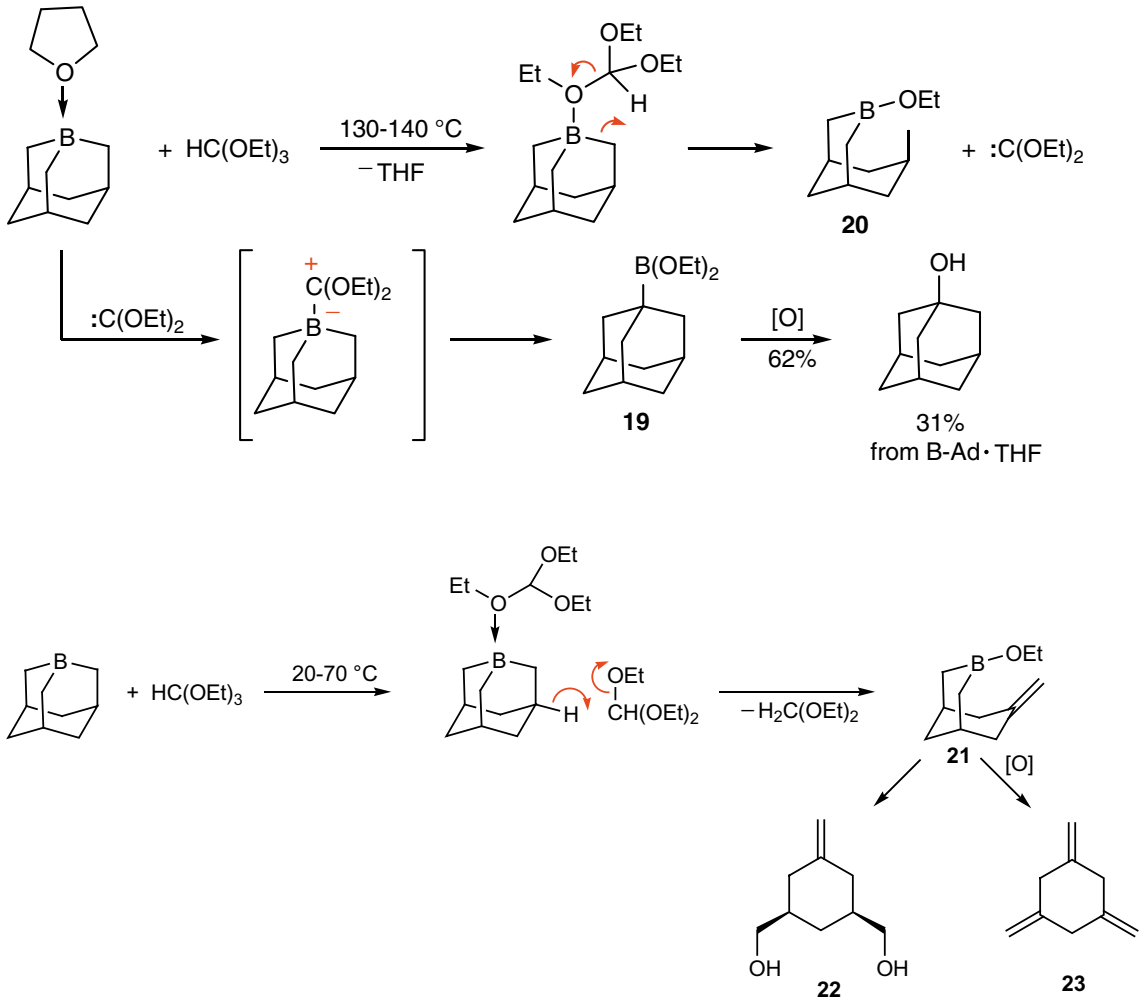
Nucleophilic diethoxycarbene **17** seems to be generated in the course of the reactions (Scheme 7). It forms the adduct with triorganoborane **18** which undergoes series of anionotropic rearrangements to the corresponding final product **16** (three R groups migrate from boron to the carbon atom and two EtO groups transfer to boron).



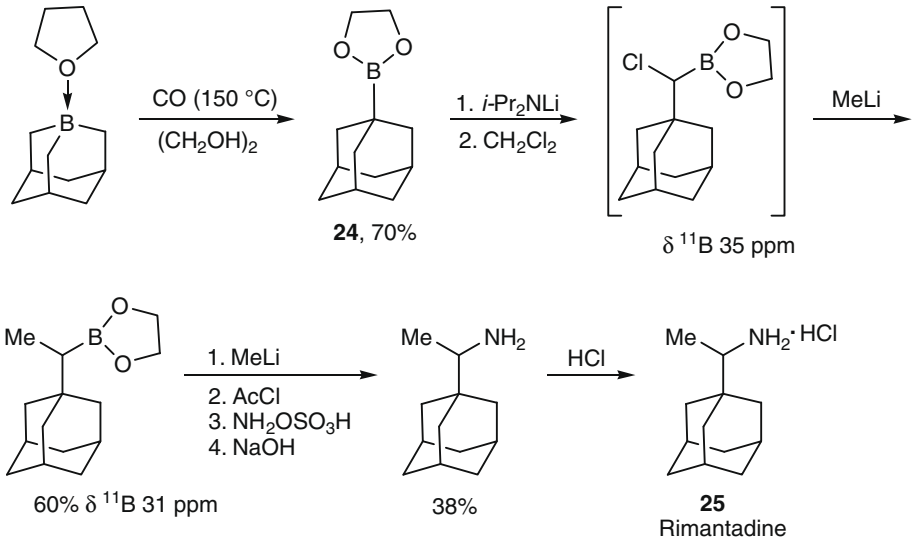
Scheme 7.

Utilization of the reaction to 1-boraadamantane derivatives revealed the different behaviour of 1-boraadamantane itself and its adduct with THF [16]. The latter reacts with orthoformate similarly to R_3B (130–140 °C) producing diethyl 1-adamantylboronate (**19**) and 3-ethoxy-7α-methyl-3-borabicyclo[3.3.1]nonane (**20**) as the result of the cleavage of adamantane core. At the same time, reaction of 1-boraadamantane itself with orthoformate proceeds at 20–70 °C via the hydride elimination leading to 3-ethoxy-7-methylene-3-borabicyclo[3.3.1]nonane (**21**) and $CH_2(OEt)_2$ (Scheme 8).

Oxidation of **21** with hydrogen peroxide in the presence of sodium hydroxide gave rise to *cis*-1,3-(hydroxymethyl)-5-methylenecyclohexane (**22**)[16]. The compound **21** was also transformed to 1,3,5-trimethylenecyclohexane (m.p. 34–35 °C), which does not isomerizes to mesitylene on keeping in a closed bottle for 10 years [7].



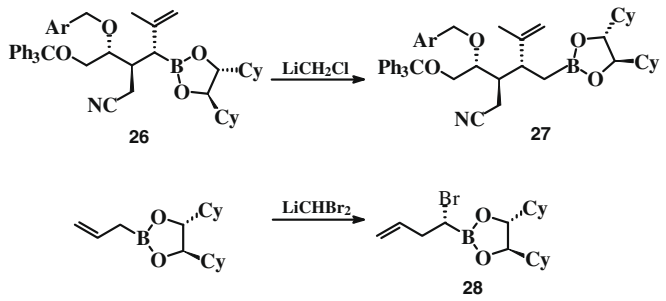
Scheme 8.



Scheme 9.

Transesterification of 1-adamantanylboronate **19** with ethylene glycol gave rise to the boronate **24**. The latter was explored as a starting material for the preparation of rimantadine (**25**), an antiviral drug (Scheme 9) [7,17].

This transformation was performed to demonstrate possibilities of boron chemistry. Application of 1-boraadamantanes in synthesis was reviewed [7,18].



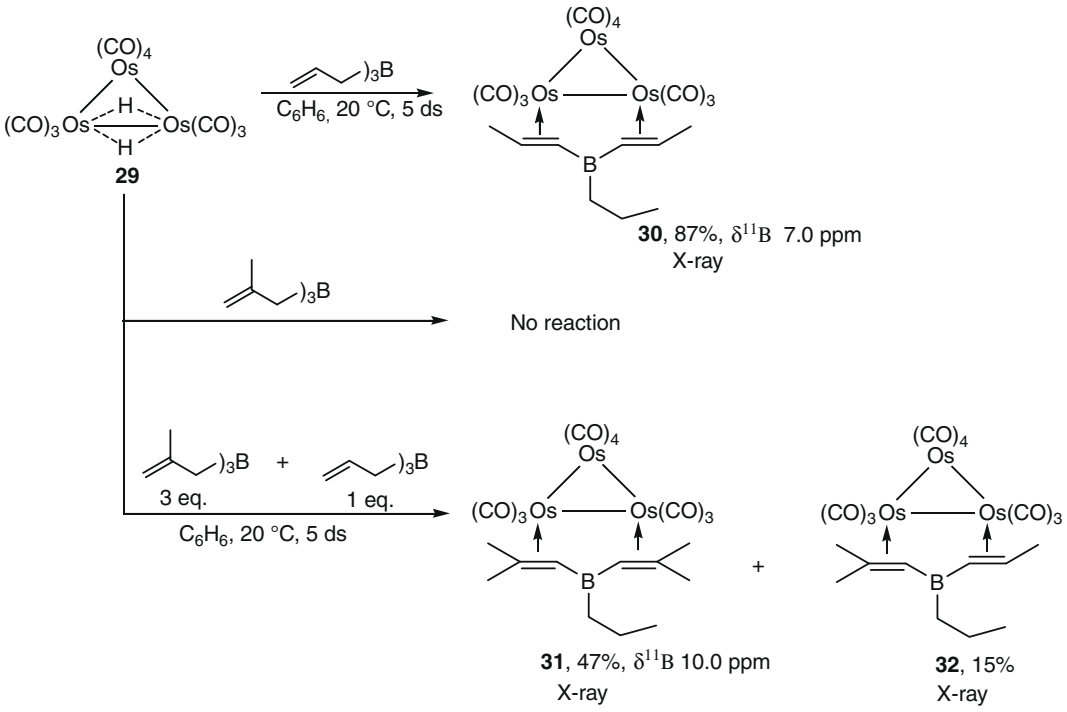
Scheme 10.

2.3. Chain extension

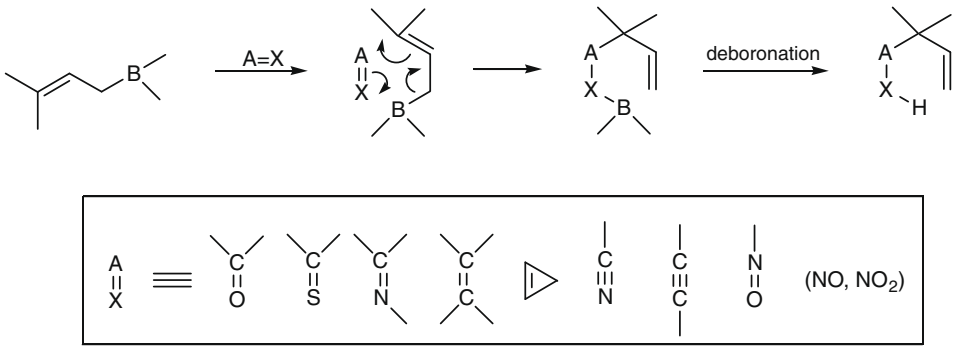
Two examples of the Matteson's chain extension proceeding with retention of configuration of allylic moiety are presented in Scheme 10: the reactions of the boronate **26** with $LiCH_2Cl$ leading to the butenyl boronate **27** and the synthesis of the chiral α-bromobutenyl boronate **28** [19,20].

3. Reactions of triallylboranes with osmium cluster

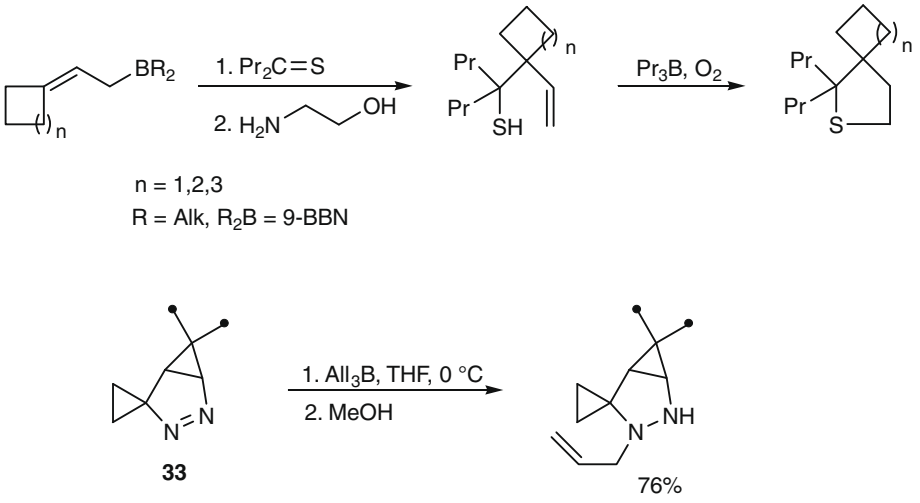
An application of allylic boranes to cluster chemistry is presented in Scheme 11 [21,22]. The reaction of triallylborane with the unsaturated 46-electron cluster $Os_3(\mu\text{-}H)_2(CO)_{10}$ (**29**) proceeds at room temperature to produce the novel symmetrical cluster **30** in 87% yield. One allylic group is reduced to propyl group and two are transformed to *trans*-propenyl fragments coordinated with osmium. This is a rare example of the isomerization of allylic boranes to vinyl counterparts.



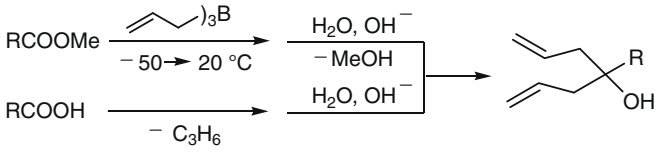
Scheme 11.



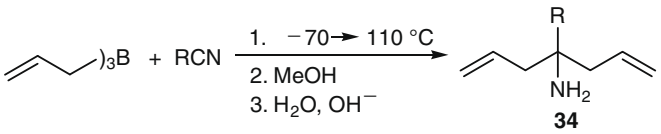
Scheme 12.



Scheme 13.



Scheme 14.



Scheme 15.

Trimethallylborane reacts with the cluster **29** only in the presence of triallylborane. Two products (**31** and **32**) are formed and the both contain propyl group. The main product **31** contains two isobutenyl groups originated from methallyls. In the minor product **32,** the boron atom is bounded with two different alkenyl groups (isobutenyl and *trans*-propenyl). Complexes **30**–**32** have been characterized by an X-ray crystallographic study.

4. Allylboration of the compounds with multiple bonds

Allylboration of organic compounds with multiple bonds discovered in 1964 (allylboration of aldehydes and ketones) [23] is to-day a general reaction [1–5] proceeding with the participation of the allylic boron system as a whole (Scheme 12) [5].

A great variety of homoallylic compounds are available via the allylboration reaction.

Two examples of monoallylboration are presented in Scheme 13: synthesis of butenyl thiols [24] and N-allylation of pyrazoline derivative **33** [25].

4.1. Diallylboration

Organic acids and esters undergo diallylboration under the action of triallylborane or allyl(dialkyl)boranes (−70 to 20 °C) to produce the corresponding tertiary alcohols (Scheme 14) [26].

In the case of acids, a rapture of one B–C bond of triallylborane takes place first producing propene. Then allylboration of the C=O fragment proceeds followed by β-elimination to form R(allyl)ketone, which immediately undergoes allylboration (for the better understanding the reactions see Scheme 18 below).

From nitriles and triallylborane, tertiary diallylated amines **34** are available in a high yield (Scheme 15).

Monoallylboration of the C≡N bond takes place at –30 to 20 °C, while an addition of the second allylborane fragment requires heating at 100–120 °C [27].

Pyrrole, pyridines and isoquinolines undergo the reductive α,α′-diallylation with triallyl- or trimetallylborane in the presence of alcohols (isopropanol), water, or RNH_2 to produce the *trans*-α,α′-diallylated N-heterocycles **35–38**, which are transformed into the corresponding *cis*-isomers (**39**–**42**) on heating with triallylborane (Scheme 16) [28].

N-Boc protected derivatives of *cis*-isomers **39**, **40** and **42** were transformed into bicyclic (**43** and **44**) and tricyclic **45** compounds via ring-closing metathesis in the presence of the Grubbs "first generation" ruthenium catalyst, $Cl_2Ru{=}CHPh(PCy_3)_2$ [28c].

Lactams containing NH fragment also undergo diallylation to give 2,2-diallylated N-heterocycles [27].

4.2. Triallylboration

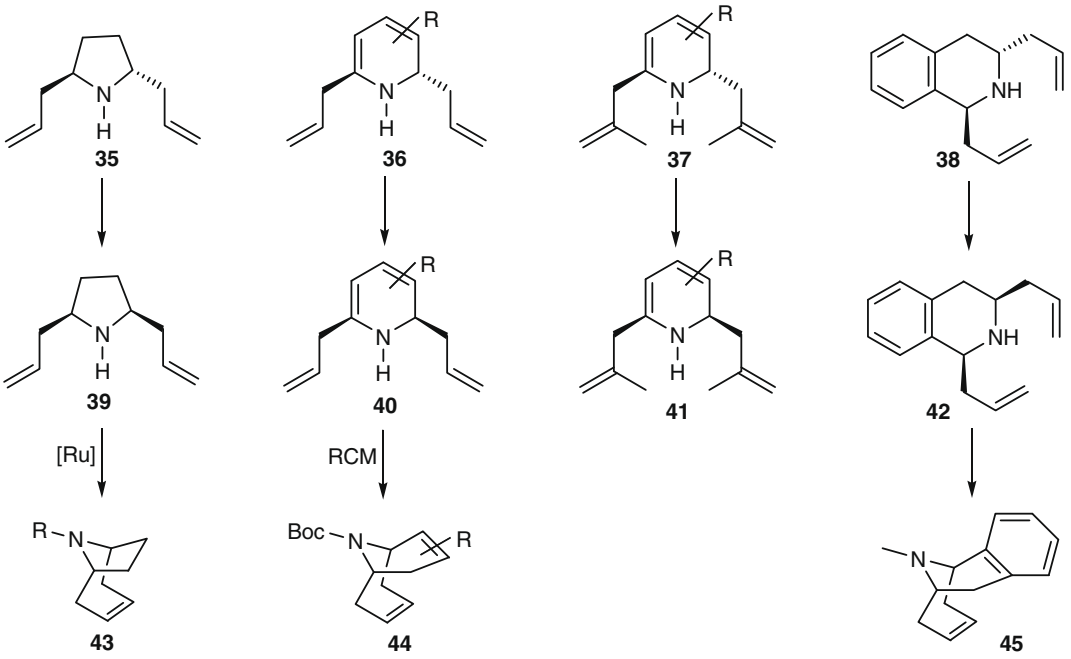
Ethylene carbamate and dialkyl cyanamides undergo triallylation on heating with triallylborane to furnish triallylmethanol and (triallylmethyl)amine, respectively (Scheme 17) [29].

Similar reaction with O,S-dimethyl xanthogenate produces triallylmethyl thiol, however it is unstable and the protection of the HS group must be applied to isolate the product.

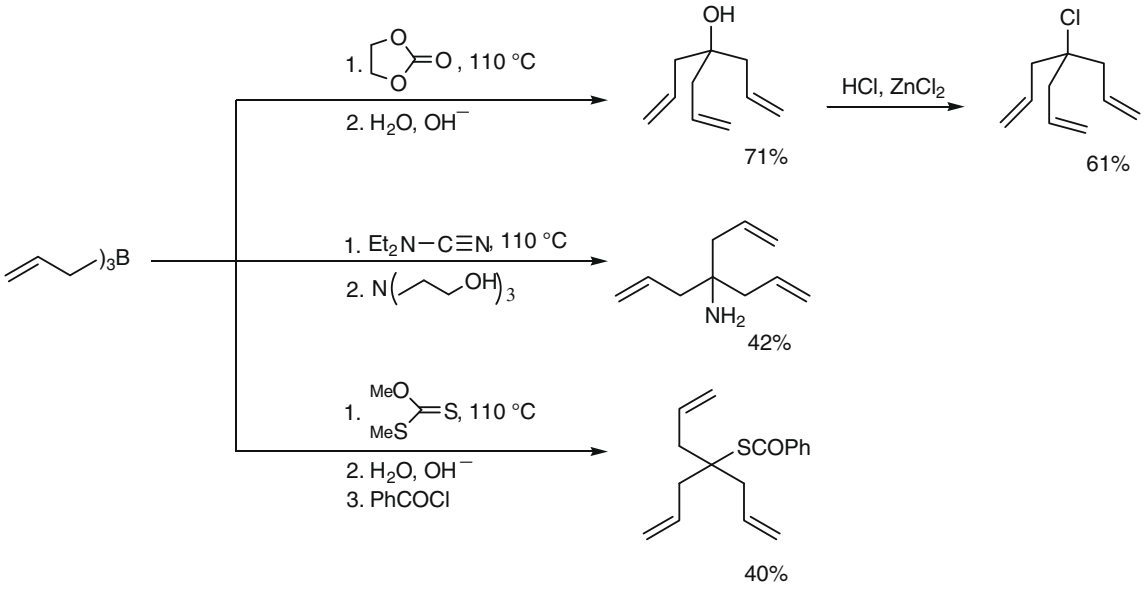
The reactions shown in Scheme 17 proceed via allylboration – β-elimination – allylboration – β-elimination – allylboration sequence (Scheme 18) [29].

5. Boron containing clathrochelates

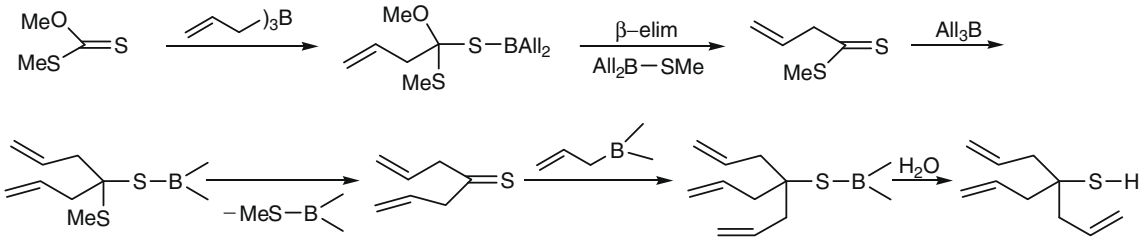
Three clathrochelate α-dioximates **46** with two apical allylborate moieties and an iron ion encapsulated in the cage of a macrobicyclic ligand are obtained by direct template condensation of acyclic and alicycle dioximes, triallylborane and tetrakis(acetonitrile)dichloroiron (II) in butanol (Scheme 19) [30]. In fact, dibutyl allylboronate is the reactive species in the condensation: two of the three B–C bonds in triallylborane are cleaved by butanol or/and dioxime.



Scheme 16.

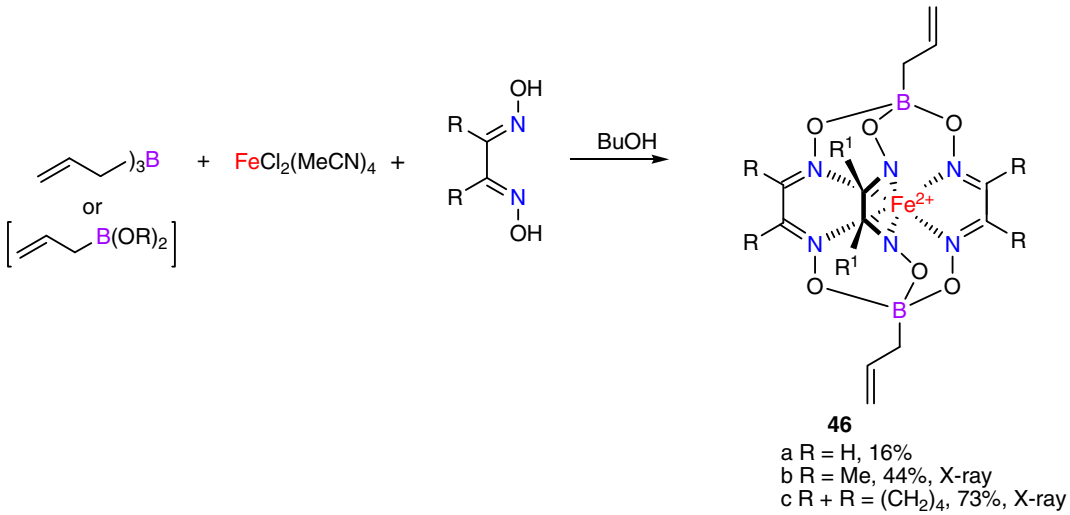


Scheme 17.



Scheme 18.

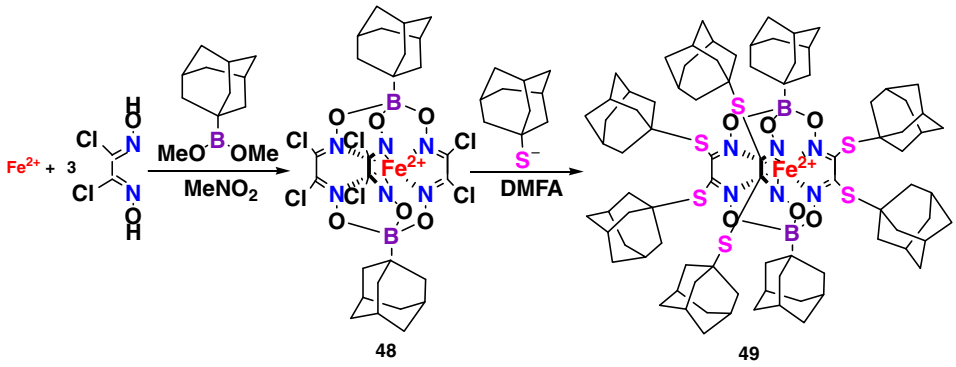
Adamantylboron-capped iron(II) clathrochelates **47** were synthesized by the interaction between $FeCl_2(MeCN)_4$, dimethyl adamantylboronate and the corresponding dioxime in nitromethane [31].



46

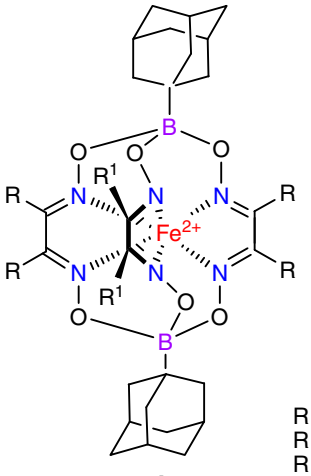
a R = H, 16%
b R = Me, 44%, X-ray
c R + R = $(CH_2)_4$, 73%, X-ray

Scheme 19.



48 **49**

Scheme 20.



47

R = Me, 20% (in MeOH)
R = Ph, 70%, X-ray
R + R = $(CH_2)_4$, 50%, X-ray
R + R = $(CH_2)6$, 65%, X-ray

The hydrophobic octaadamantylated clathrochelate **49** was obtained by a complete nucleophilic substitution of six reactive chlorine atoms in the precursor **48** available from the direct template reaction of dichloroglioxime and 1-AdB$(OMe)_2$ on iron(II) ion matrix, [$FeCl_2(MeCN)_4$] (Scheme 20) [31].

Substitution reaction with potassium adamantylthiolate in DMF) gave rise to the target product **49** in low yield (11%) due to the steric hindrances. At the same time, similar substitution reaction in the case of the phenylboronic hexachloride (**48,** Ad=Ph) proceeds readily to give Fe[$((AdS)_2Gm)_3(BC_6H_5)_2$] in 80% yield [31].

Tris–dioximate iron(II) clathrochelates with apical and/or ribbed hydrophobic adamantyl groups can find application for membrane transport of encapsulated metal ions. Potential applications of various clathrochelate have been reviewed [32].

Acknowledgements

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