

## Selective reactions of minor tautomers among allylic type triorganoboranes

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### Abstract

Due to the facile 1,3-B sigmatropic shifts and other skeletal rearrangements facilitated by the 2p atomic orbital of the boron atom, fast equilibria between several tautomeric forms are characteristic for allylic triorganoboranes. Spectrally the most thermodynamically stable isomers are observed, whereas the minor more reactive tautomers often participate in chemical transformations. © 1999 Elsevier Science S.A. All rights reserved.

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Unsaturated triorganoboranes, and in particular allylic type triorganoboranes show a very specific example of structural lability. Facile 1,3-B shift (reversible migration of a R<sub>2</sub>B group from position 1 to position 3 in an allylic system) in allylboranes [1] is the only known truly intramolecular allylic rearrangement, since for other allylic organometallic derivatives similar transformations are intermolecular, as for zinc and aluminium [2], require the catalysis by Lewis acids (allyltin and allylmercury compounds) [3] or proceed with very high activation barriers (silicon and germanium allyls) [4].

Fast intramolecular 1,3-migrations of dialkylboryl groups lead to almost immediate establishment of thermodynamic equilibrium among all possible allylic isomers. Very often only one, the most stable isomer can be observed experimentally by spectral methods. If two or more isomers are comparable in stability, they become tautomers, interconverting reversibly via 1,3-B shifts. Such equilibria can be studied experimentally by NMR spectroscopy [5–9].

However, the most thermodynamically stable isomer is usually not the most reactive one. This fact is responsible for the peculiar chemical properties of polyunsaturated triorganoboranes, which we encountered during

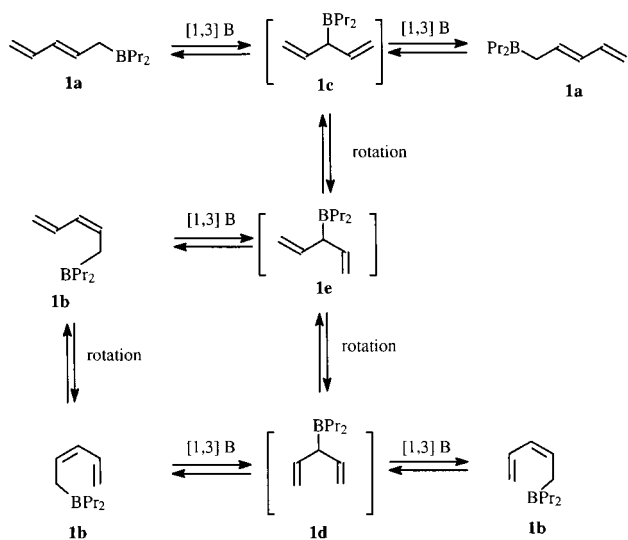
our recent studies of the intramolecular dynamics in allylic type triorganoboranes [5–9,11–14]. This account summarizes our findings in this area.

The simplest example of the selective reactivity of a minor tautomer for allylboranes was observed for 2,4-pentadienyl(dipropyl)borane **1**. In this compound *E*- and *Z*-isomers interconvert via consecutive 1,3-B shifts and intramolecular rotations (Scheme 1).

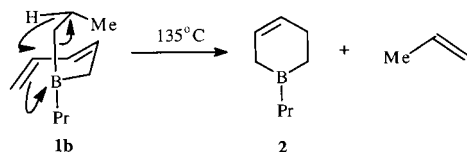
The equilibrium concentration of the *Z*-isomer **1b** is approximately 20%. However, thermolysis of **1** at 135°C gives 3-borinene **2** with 40% yield (Scheme 2). Owing to geometric considerations only **1b** can participate in this transformation. Since the yield of **2** is greater than the equilibrium content of **1b**, it is clear that when the *Z*-isomer is consumed, it is reformed from the *E*-isomer (**1a**) by the mechanism shown in Scheme 1.

In 2,4,6-heptatrienyl(dipropyl)borane **3** the observed equilibria involve all four possible isomers with the terminal placement of the dipropylboryl group **3a–d** [7]. Similarly to the previous case, **3a–d** interconvert reversibly via various combinations of 1,3-B migrations and intramolecular rotations with the intermediacy of the relatively unstable isomers **3e,f**. The equilibrium content of the *Z,Z*-isomer **3d** is 1%. However, a 1,7-hydrogen sigmatropic shift occurs only in **3d** giving rise to the vinylic type triorganoborane **4** (two isomers (**4a:4b**) in the ratio 95:5) [7] (see Scheme 3).

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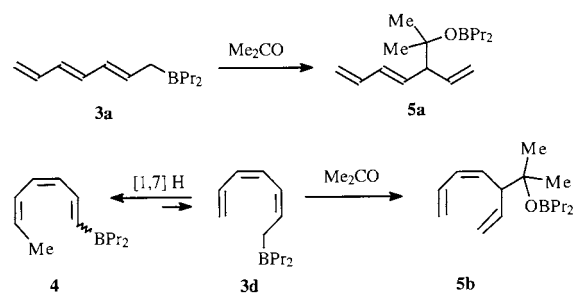


Scheme 1.



Scheme 2.

The resulting equilibrium mixture obtained after 2 h at  $100^\circ\text{C}$  contains 92% of **4** and 8% of **3**. Again the whole transformation proceeding via the minor isomer **3d** becomes possible due to the facile 1,3-B migrations occurring in **3** and interconverting reversibly the isomers **3a–d**. We used this phenomenon for the first synthesis of isomerically pure *Z,Z*-1,3,5-heptatriene by the reaction of **4** with acetic acid [8].

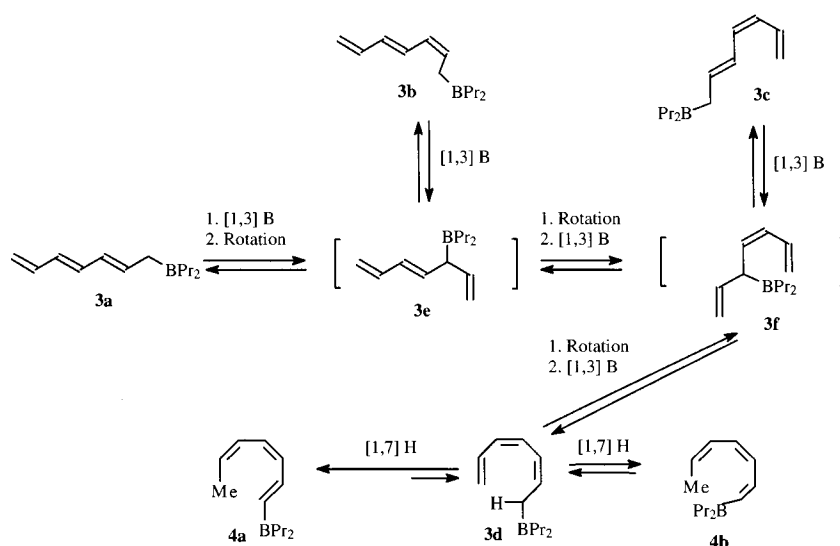


Scheme 4.

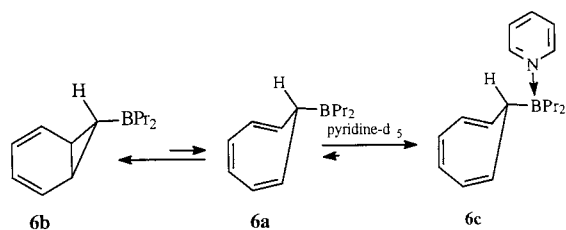
Interestingly, the same principle can be realized in the reverse order. Thus, whereas the reaction of **3** with acetone gives mainly the *E*-isomer **5a** of the expected borinic ester, the same reaction with **4** leads to isomerically pure *Z*-isomer **5b** (Scheme 4). In the latter case acetone reacts with **3d**, which forms from **4** via 1,7-H shift and is trapped in the excess acetone before it could rearrange into more stable isomers **3a–c** [7].

A clear example of the selective reactivity of a minor isomer gives the cycloheptatrienyl(dipropyl)borane **6** [9]. This compound exists as an equilibrium mixture of tropyliene and norcaradiene valence tautomers **6a** and **6b**. The latter compound predominates significantly: at  $-120^\circ\text{C}$  the ratio **6a:6b** is 1:180, whereas at  $25^\circ\text{C}$  the content of **6a** is about 30%. Nevertheless, independently of the temperature regime only **6a** reacts with deuteropyridine to give complex **6c**, since in **6b** the unoccupied 2p atomic orbital of boron is involved in the conjugation with the Walsh orbital of the cyclopropane moiety, and its affinity for an electron pair is much lower [9] (see Scheme 5).

All known cyclononatetraenes rearrange quantitatively into corresponding dihydroindenes at temperatures higher than  $0^\circ\text{C}$  [10]. Only in the case of the



Scheme 3.

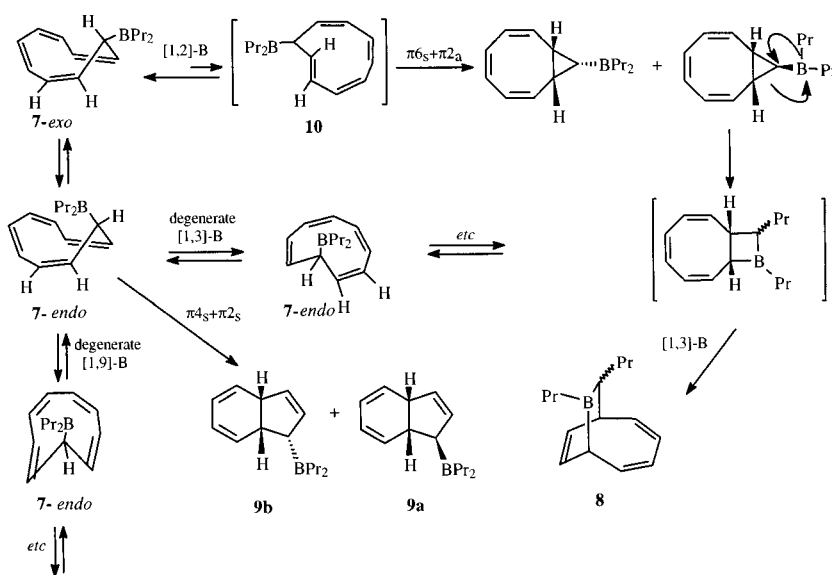


Scheme 5.

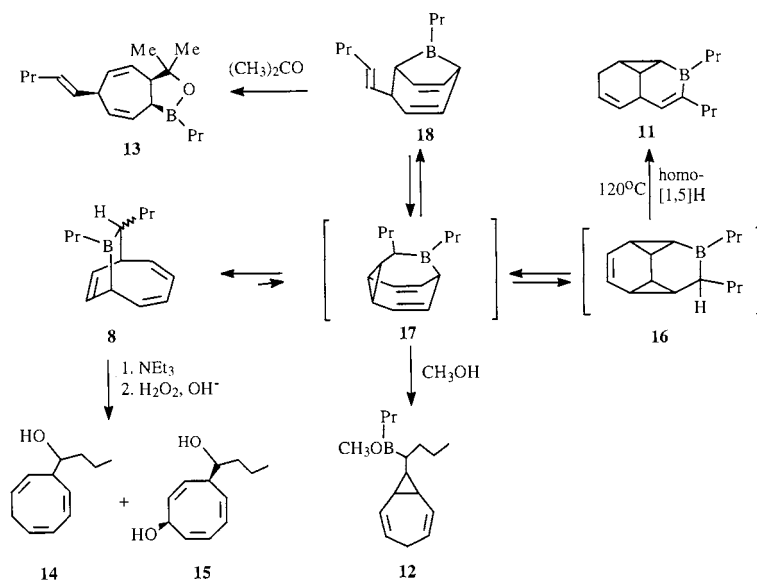
boron compound **7** is the main product of the rearrangement under the same conditions different. With the bicyclic structure **8** [11–13]. The corresponding dihydroindenes **9a,b** are found in the reaction mixture as side

products (about 10%). The main property of **7**, allowing it to rearrange by this unusual pathway, is again the facile sigmatropic migrations of the dipropylboryl group. Three different sigmatropic migrations of the  $\text{Pr}_2\text{B}$  group proceed in **7** (Scheme 6): degenerate 1,3-B and degenerate 1,9-B shifts in **7-endo** and rearrangement into the mono-*trans*-compound **10** via the 1,2-B migration in **7-exo** [11b]. Although **10** is  $6.5 \text{ kcal mol}^{-1}$  less stable than **7**, it serves as a key intermediate in the whole transformation resulting in **8** (Scheme 6) [11,12].

The most interesting chemical behavior was observed for the bicyclic borane **8** [14]. Various chemical transformations of **8** gave selectively the products with completely different hydrocarbon frameworks (Scheme 7).



Scheme 6.



Scheme 7.

Thus, thermolysis gives tricyclic borane **11**, methanolysis provides borinic ester **12** with the bicyclo[5.1.0]octadiene skeleton, whereas the reaction of **8** with acetone results in the borinic ester **13** with the (1-pentenyl)-cycloheptadiene structure of the carbon skeleton. Remarkably, only the oxidation of **8** with basic hydrogen peroxide in the presence of an excess of triethylamine, i.e. under conditions when the empty 2p atomic orbital of boron is blocked, provided the mixture of compounds **14** and **15**, each with the expected cyclooctatriene structure [14].

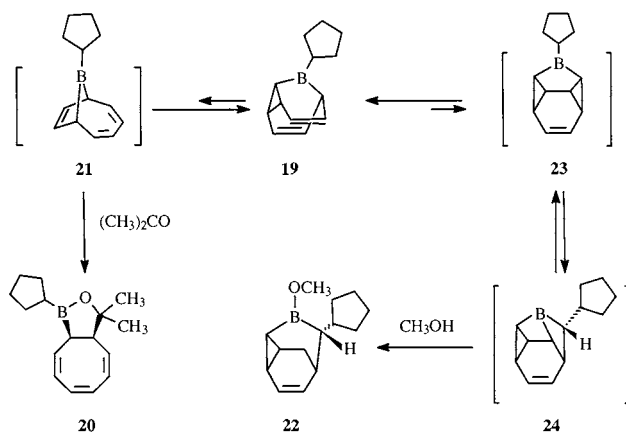
The dramatic difference in the structures of the products from the various chemical transformations of borane **8** may be explained by the trapping of minor valence tautomers of **8**. Thus, the results of the thermolysis may be accounted for a homo[1,5]-H sigmatropic shift in tetracyclic borane **16** (Scheme 7); transformations very similar to the equilibrium between **8** and **16** are well documented for (CH)<sub>10</sub> hydrocarbons. In the same fashion the structures of the borinic esters **12** and **13** imply the intermediacy of borabullvalene **17** and bicyclic borane **18**, respectively, the latter being a product of cyclopropylmethyl-butenyl rearrangement in **17** [14].

Trapping of minor valence tautomers is well documented [15] (see also examples above); however, the reactions of borane **8** provide according to our knowledge the first example when *several different* minor valence tautomers are selectively trapped. We called this phenomenon the *diverse chemoselectivity* of borane **8**.

It should be noted that not only 1,3-B shifts, but at least two more skeletal rearrangements are involved in the equilibria between **8**, **16**, **17** and **18**. On the other hand, to provide the observed selectivity all of these reactions should proceed very fast. Therefore one can conclude that the orbital assistance of the unoccupied 2p atomic orbital of boron can facilitate such rearrangements. This is in accord with the similar recent observation [16].

Another example of diverse chemoselectivity has been found for 9-cyclopentyl-9-borabarbaralane **19** (Scheme 8) [17]. Reactions of **19** with carbonyl compounds and deuterioacetic acid apparently proceed via borane **21**. On the other hand, methanolysis of **19** gives cleanly borinic ester **22**, that implies the intermediacy of **23** and **24** (Scheme 8) [17].

It is interesting to note that the equilibria between **19**, **21** and **23** are realized through the same rearrangements as the equilibria between **8**, **16** and **17**. The corresponding boranes **8** and **21**, **17** and **19**, **16** and **23** may be regarded as differentially substituted homologues. For the compounds Pr<sub>2</sub>C<sub>9</sub>H<sub>9</sub>B (**8**, **16**, and **17**) the most stable tautomer **8** has the cyclooctatriene structure of the hydrocarbon skeleton. Such a framework is stabi-



Scheme 8.

lized by overlap of 2p atomic orbital of boron with the  $\pi$ -system of double bonds suggested by the relatively low value of  $\delta^{11}\text{B}$  (70.2 ppm). For the compounds (*cyclo*-C<sub>5</sub>H<sub>9</sub>)C<sub>8</sub>H<sub>8</sub>B (**19**, **21**, **23**) the most stable isomer **19** has the structure of borabarbaralane, since in **21** due to the skeletal strain the overlap of 2p atomic orbital of boron with the  $\pi$ -system is impossible. The chemical shift of boron in **19** has the value typical for triorganoboranes ( $\delta^{11}\text{B}$  = 80.2 ppm), this borane is much more reactive compared to **8**. Whereas the transformations **8** → **12** and **8** → **13** require overnight reaction at ambient temperature, the reactions of **19** with methanol and acetone proceed within seconds at  $-30^\circ\text{C}$ . Note that boranes (R<sub>2</sub>N)BC<sub>8</sub>H<sub>8</sub> with the structure of **21** were characterized as the kinetic products of borylation of the cyclooctatetraenide dianion [18,19], which can be either thermally or photochemically converted to corresponding borabarbaralanes [19]. This fact supports our point of view that the unoccupied 2p atomic orbital of boron facilitates the rearrangements like **19** → **21**.

In conclusion, we would like to point out that the diverse chemoselectivity found for boranes **8** and **19** provides an unique opportunity for the analysis of the transition states for the corresponding reactions. If the reasons for the selective reactions of a minor tautomer are quite apparent in such simple cases as 2,4,6-hepta-trienyl(dipropyl)borane **3**, in two latter cases such reasons are obscure at the moment. The high-level computational studies of the diverse chemoselectivity are underway in our group.

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