Unusual Chemical Behavior of 9,10-Dipropyl-10-borabicyclodeca-2,4,7-triene, Heteroanalog of $(CH)_{10}$ Hydrocarbons

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The title compound **1** selectively gives products with completely different carbon skeletons in various reactions. Thus, thermolysis of **1** provides tricyclic borane **4**, oxidation leads to the compounds **5**, **6** (in a 5:1 ratio) with cyclooctatriene structure, methanolysis followed by oxidation yields bicyclic alcohol **7**, and the reaction of **1** with acetone leads to the product with the cycloheptadiene skeleton **8**. Such unusual chemical behavior of **1** can be rationalized by its coexistense with minor valence tautomers **12, 17, 18, 22**.

Introduction

The bountiful and unusual chemistry of the $(CH)_{10}$ hydrocarbons and related systems has enticed the attention of experimental chemists and challenged theoreticians for the three last decades.[1] The interconversions of these compounds are various and confusing, but, on the other hand, they are strictly selective and regular. Nevertheless, a complete understanding of the mechanisms of these reactions has not yet been achieved.

Recently we prepared cyclononatetraenyldipropylborane[2] and studied its rearrangements at ambient temperature.[2,3] It was found that, as a result of the combination of several rearrangements, a mixture of three boranes **1**−**3** in a 10:1:2 ratio is obtained after distillation of the reaction mixture (Scheme 1).

The main product, 9,10-dipropyl-10-borabicyclodeca-2,4,7-triene (**1**) is a structural analog of $(CH)_{10}$ hydrocarbons. The present work deals with the study of the unusual chemical properties of this compound.

Results and Discussion

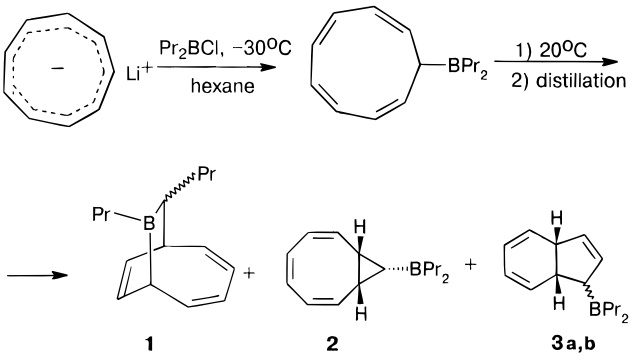
The salient feature of the chemical behavior of compound **1** is the selective formation of products with principally different skeletons upon treatment with different reagents (Scheme 2, Figure 1). Thus, thermolysis of **1** smoothly gives tricyclic borane **4** and oxidation leads to the expected products **5**, **6** (in a 5:1 ratio) with an eight-membered cycle; methanolysis followed by oxidation selectively yields the bicyclo[5.1.0]octadienic alcohol **7**, whereas the reaction with acetone results in the product with the heptadiene skeleton **8**.

The chemical transformations of compound **1** were studied using the mixture of compounds **1**−**3** (in a 10:1:2 ratio).[2,3]

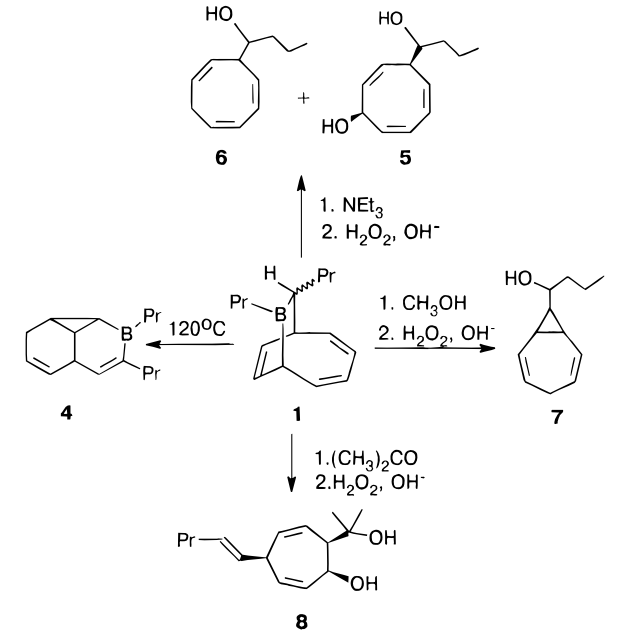
Thermolysis of Compound 1. Heating compound **1** at 120 °C for 2 h in a sealed tube quantitatively gives vinylic borane **4**. Compounds **3a,b** remained unchanged under these conditions. The structure of compound **4** was unambiguously assigned by 2D correlation NMR spectroscopy and confirmed chemically by the deboration with acetic acid, which gave the expected 2-pentenyl-3-norcarene **9** (Scheme 3).

It is known that the carbon analog of **1**, hydrocarbon **10**, undergoes a degenerate thermal rearrangement *via* the tetracyclic compound **11** (see Scheme 4). Apparently,

Scheme 1



Scheme 2



[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) (a) Scott, L. T.; Jones, M. J. *J. Chem. Rev.* **1972**, *72*, 181−202. (b) Otter, A.; Sabbioni, G.; Neunschwander, Kellerhalls, H. P. *Helv. Chim. Acta* **1986**, *69*, 124−135. (c) Hassenruch, K.; Martin, H. D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125−1146. (d) Chai, S.; Neunschwander, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 973−975.

(2) Gurskii, M. E.; Gridnev, I. D.; Buevich, A. V.; Bubnov, Yu. N. *Organometallics* **1994**, *13*, 4658−4660.

(3) Gridnev, I. D.; Gurskii, M. E.; Buevich, A. V.; Bubnov, Yu. N. *Russ. Chem. Bull.* **1996**, 107−114.

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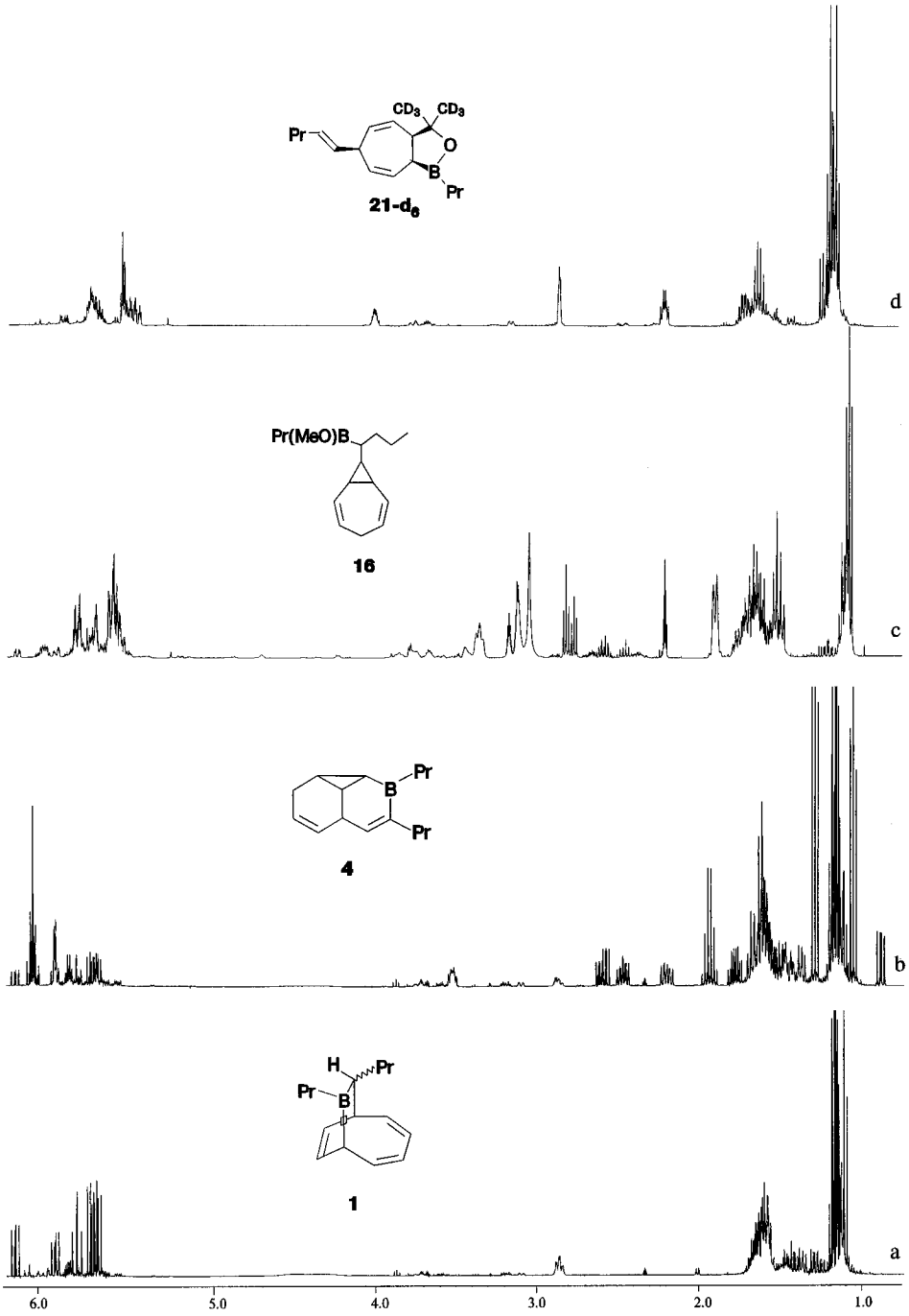
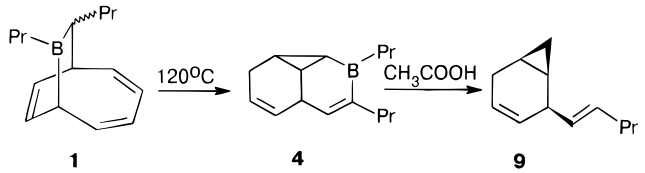


Figure 1. ^{1}H NMR spectra (400 MHz) illustrating the dramatic changes in the structure of **1** (a) under thermolysis (b) and in the reactions with methanol (c) and deuteroacetone (d).

Scheme 3. Thermolysis of Compound 1



1 **4** **9**

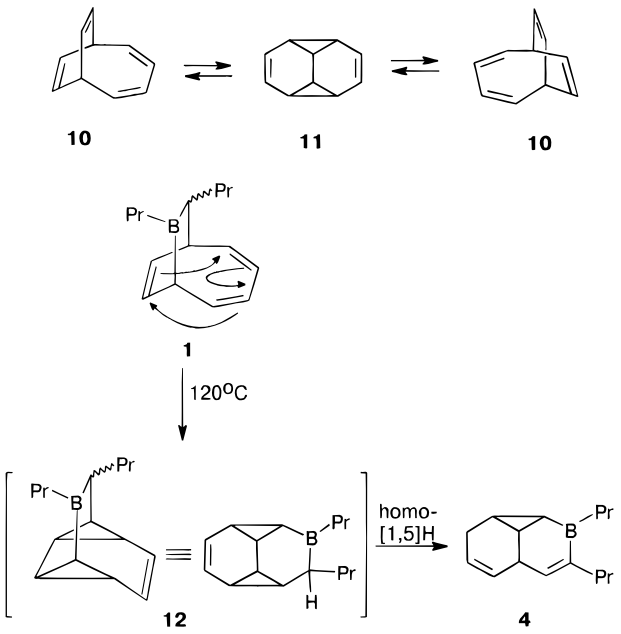
the boron tetracycle **12** can also form upon heating compound **1**, while the final thermolysis product **4** can be the result of the [1,5] homodienyl hydrogen shift in **12**. The driving force of the latter rearrangement is the formation of a thermodynamically stable boron-vinyl fragment in **12** (Scheme 4).

Oxidation of Compound 1. The treatment of the mixture of compounds **1**−**3** with excess triethylamine at −30 °C followed by oxidation with H_2O_2, extraction, and evaporation of solvents gave a mixture of compounds **5, 6**, **13, 14** (in a 2:3:1:1 ratio), which were separated by column chromatography (Scheme 5). The structures of compounds **5**, **6**, **13**, and **14** were adequately established by the use of 2D NMR correlation spectroscopy and confirmed by IR and high resolution mass spectral data.

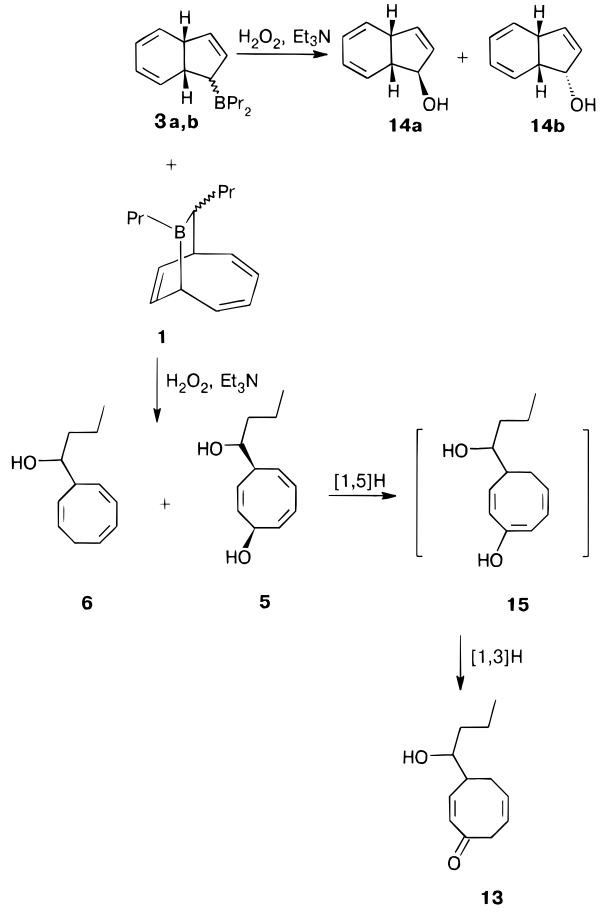
Diol **5** is the product of direct oxidation of two B−C bonds in **1**. Compound **5** undergoes a sigmatropic [1,5] hydrogen shift[4] resulting in enol **15**, and ketonization of the latter gives compound **13**. This was confirmed by a special experiment, *viz.*, compound was **15** completely transformed to **13** after storing for 20 h at room temperature. Trienic alcohol **6** is formed *via* a subsequent

(4) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187−217.

Scheme 4. Comparison of the Degenerate Thermal Rearrangement in Bicyclo[4.2.2]deca-2,4,7,9-tetraene (10)[5] and Thermolysis of 1



Scheme 5. Oxidation of Compounds 1 and 3a,b

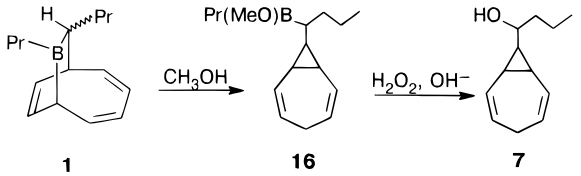


hydrolysis−oxidation of compound **1**, which indicates that at the first stage the oxidation of **1** competes with the hydrolytic cleavage of the allylboron fragment.[6]

The dihydroindene alcohols **14a,b** are formed as the result of oxidation of compounds **3a,b**. The product corresponding to the oxidation of compound **2** was not isolated, probably due to its low content in the reaction mixture.

Reaction of Compound 1 with Methanol. Organoboranes of the allylic type are known to react readily with alcohols with allylic rearrangement[6] giving the corresponding unsaturated hydrocarbons. Therefore, the methanolysis and subsequent oxidation of compound **1** was expected to result in an alcohol with the eight-membered ring **6** (Scheme 5). Formation of some of this product was already observed during the oxidation. However, the product isolated by distillation had a completely unexpected structure. The analysis of the $^1H-^1H$ COSY spectrum of the sample containing 10 mol % of $Eu(fod)_3$ allowed us to determine the structure of the methanolysis product, which turned out to be 8-(1-hydroxybutyl)bicyclo[5.1.0]octa-2,5-diene (**7**).

Scheme 6. Methanolysis−Oxidation of Compound 1



It is worth noting that the carbon skeletons of alcohol **7** and starting compound **1** differ considerably. The detailed analysis of the NMR spectra of the reaction mixture showed that borinic ester **16** is a direct product of the methanolysis (Scheme 6), *i.e.*, ***a dramatic transformation of the carbon skeleton takes place in the course of the reaction***. Moreover, besides borinic ester **16** and some amount of dihydroindene (product of methanolysis of borane **3**), not more than 5% of unidentified products could be detected, and, therefore, the chemoselectivity is about 95%.

Since the methanolysis of allylic type organoboranes proceeds with allylic rearrangement, the direct precursor of borinic ester **16** should have structure **17**. Therefore one can propose that **17** is a valence tautomer of **1**, and the rate of the reaction of **17** with methanol is much higher than that of **1** (Scheme 7). Chemoselectivity derived from minor isomers that are not even observable spectrally is not unusual in cycloaddition reactions of polyunsaturated cyclic compounds.[7] This phenomenon has been used for the detection of a nonobservable tautomeric form.[8] Therefore the results of the methanolysis of borane **1** confirm its tautomerism with **17**.

It is interesting to note that the observed skeleton reconstruction has direct analogies in the chemistry of $(CH)_{10}$ hydrocarbons. Hydrocarbon **10** is known to give smoothly bullvalene **19** by the photolysis at room temperature (Scheme 7),[9] while the latter in turn can transform to isobullvalene **20**.[1] The rearrangement of **18** to **17** should occur much faster than the transforma-

(5) (à) Jones, M., Jr.; Reich, S. D.; Scott, L. T. *J. Am. Chem. Soc.* **1970**, *92*, 3118−3126. (b) Jones, Jr., M.; Reich, S. D.; Scott, L. T., Sullivan, L. E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 644−645.

(6) Mikhailov B. M.; Bubnov Yu. N. *Organoboron Compounds in Organic Synthesis*; Harwood Acad. Sci. Publ.: London, New York, 1984.

(7) Paquette, L. A. *Tetrahedron* **1975**, *31*, 2855−2883.

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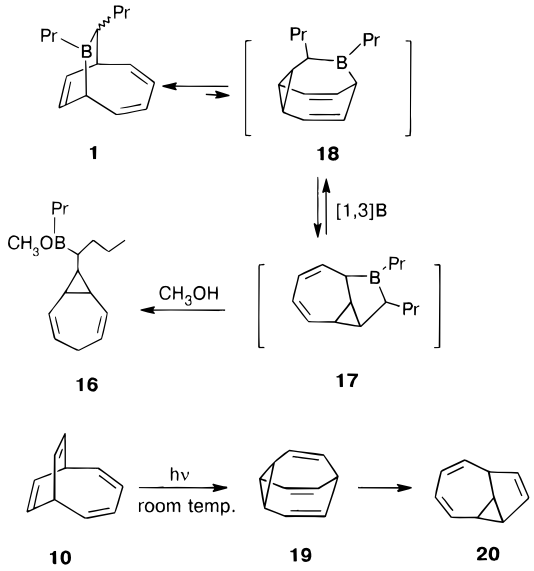
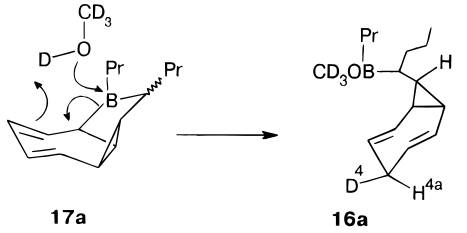
(9) (a) Jones, M., Jr.; Scott, L. T. *J. Am. Chem. Soc.* **1967**, *89*, 150−153. (b) Doering, W. v. E.; Rosenthal, J. W. *Tetrahedron Lett.* **1967**, 349−352.

(10) Bubnov, Yu. N. *Pure Appl. Chem.* **1987**, *59*, 895−898.

Scheme 7. Comparison of the Methanolysis of 1 with the Known Rearrangements in 10



Scheme 8. Mechanism of the Formation of Deuteromethanolysis Product 16a



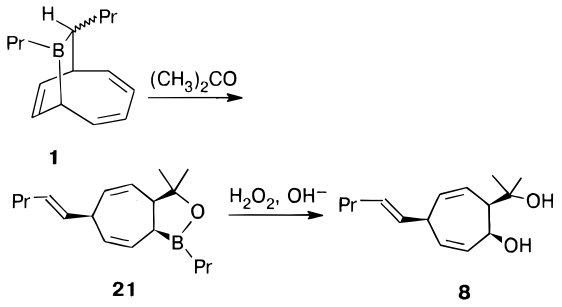
tion of **19** to **20**, because a [1,3] boron shift is much more facile than a [1,3] carbon shift.[2,4]

The treatment of compound **1** with deuteromethanol gave selectively one isomer of the corresponding borinic ester **16a** (according to ^{13}C NMR spectrum of the reaction mixture). In the ^{1}H NMR spectrum of **16** the protons of the geminal pair of H-4 and H-4a can be distinguished by the values of their coupling constants from the H-3 and H-7 protons. The proton H-4 has an allylic coupling constant $^{3}J = 7.0$ Hz, while for the proton H-4a the same coupling does not exceed 1.5 Hz. The molecular modeling shows that the proton H-4 is *exo*-disposed relative to cyclopropane ring, and the proton H-4a occupies *endo*-position. The comparison of the spectra of **16** and **16a** indicates that the signal of the proton H-4 is absent in the spectrum of **16a**. Therefore, the product of deuteromethanolysis has the structure shown in Scheme 8, which is in a good agreement with the above proposed mechanism.

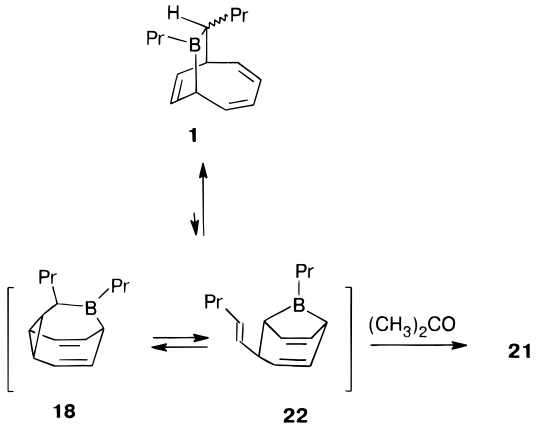
Reaction of Compound 1 with Acetone. Borane **1** readily reacts with acetone at room temperature to give borinic ester **21** as a single product (Scheme 9). The subsequent oxidation of the reaction mixture results in diol **8**. The structure of compound **8** was adequately established by 2D correlation NMR spectroscopy and confirmed by IR and HRMS. Figure 1 demonstrates a high chemoselectivity of the reaction; besides the signals of the main product **8**-d_6, only signals of the corresponding substituted dihydroindenes (products of the reaction of **3** with deuteroacetone) can be detected in the spectrum.

Considering the structure of **21** together with the fact that allylboranes always react with ketones with allylic

Scheme 9. Reaction of Borane 1 with Acetone



Scheme 10



rearrangement,[6,10] one can conclude that it is bicyclic borane **22** that enters the reaction with acetone (Scheme 10). Compound **22** may be formed as a result of cyclopropylmethyl−butenyl rearrangement in borabullvalene **18**.

As in the reaction of **1** with methanol, in the reaction of **1** with acetone, a dramatic reorganization of the carbon skeleton of the starting molecule takes place. According to the previous discussion, that means that compound **22** is also a minor tautomer of **1** not observed in the spectra (Scheme 10).

Discussion

The results of the thermolysis of borane **1** and its reactions with methanol and acetone indicate complex dynamic properties of **1**. A series of tautomeric forms, *viz.* **1, 12, 17, 18,** and **22**, coexist at room temperature, reversibly rearranging into each other *via* electrocyclic reactions, Cope rearrangements, and sigmatropic shifts. At the same time only the signals of compound **1** are observed in the NMR spectra, which proves its relatively high thermodynamic stability. The latter can be accounted for by the p-π homoconjugation of the unoccupied 2p-AO of the boron atom and the π-system of the double bonds in **1**. The existence of such orbital interaction is supported by the unusually low value of the ^{11}B chemical shift in compound **1** (70.2 ppm, whereas 85 ppm is the usual value for allylic type triorganoboranes[11]). A similar effect of the p-π homoconjugation on the δ ^{11}B in borabicyclic compounds was previously reported.[12]

The same orbital interaction can be also a reason of the relatively low activity of the bicyclic compound **1** itself

(11) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, Heilderberg, New York, 1978.

(12) Schulman, J. M.; Disch, R. L.; Schleyer, P. v. R.; Bühl, M.; Bremer, M.; Koch, W. *J. Am. Chem. Soc.* **1992**, *114*, 7897−7901.

in the reactions with methanol and acetone. The same conclusion should be valid for borabullvalene **18**, in which p-π homoconjugation is also possible. Therefore the selective reactions of the minor tautomeric forms is quite understandable. However, the different chemoselectivity in the reactions of **1** with methanol and acetone is very difficult to rationalize. Usually very similar mechanisms are proposed for the reactions of allylboranes with alcohols and ketones, *viz*. six-membered transition states with the coordination of the boron atom on the oxygen atom of the reagent.[6,10] Therefore the selective reactions of **17** with methanol and of **22** with acetone indicate that the transition states in the reactions of allylboranes with alcohols and ketones can differ more greatly than is presently thought.

As it was noted above, the interconversions of the boranes **1**, **12**, **17**, **18**, and **22** are very similar to the rearrangements in the series of hydrocarbons $(CH)_{10}$.[1] The main distinctive feature of the rearrangements of the boron analogs is the facility of all of the conversions, which appear to proceed at room temperature with high rates. Similar to the facile [1,3] boron shift, this feature can be accounted for by the orbital assistance of the unoccupied 2*p*-AO of the boron atom.

Experimental Section

All experiments were performed under a dry argon atmosphere using absolute solvents. NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHz for ^{13}C. IR spectra were obtained in CCl_4.

Thermolysis of the Mixture of Compounds 1, 2, and 3a,b. A 1.7 g amount of the mixture of **1**, **2**, **and 3a,b** was heated in a sealed tube at 120 °C for 2 h. After this compounds **3a,b** remained unchanged, and compounds **1** and **2** rearranged quantitatively to **3,4-dipropyl-3-boratricyclo[4.4.0.^{1,6}0.^{2,10}]-deca-4,7-diene (4):** IR (cm^{-1}) ν: 1600 (B—C═C); 3030 (C═C—*C*—*H*). ^{1}H NMR (400 MHz, toluene-d_8) δ: 0.85 (dd, H-2, ^3J = 10.1, 7.7 Hz); 1.02 (t, 3H, CH_3); 1.09 (m, 2H, CH_2); 1.28 (t, 3H, CH_3); 1.46 (dm, 1H of CH_2); 1.57 (m, 2H, CH_2); 1.64 (dddd, 1H, H-10, ^3J = 10.1, 8.8, 8.8, 5.4 Hz); 1.78 (ddd, 1H, H-1, ^3J = 8.8, 7.9, 7.7 Hz); 1.91 (m, 2H, CH_2); 2.16 (m, 1H of CH_2); 2.42 (m, 1H of CH_2); 2.59 (m, 1H of CH_2); 3.49 (ddd, 1H, H-6, ^3J = 7.9, 6.1, 5.3 Hz); 5.95 (d, 1H, H-5, ^3J = 5.3 Hz); 6.12 (strongly coupled AB system of H-7 and H-8). ^{13}C NMR (50 MHz, toluene-d_8) δ: 14.8 (CH_3); 15.5 (br, C-2), 18.0 (CH_3); 22.6 (C-10); 23.3 (C-1); 24.6 (C-9); 24.9, 25.3 (2 CH_2); 29.3 (br, CH_2B); 35.5 (C-6); 38.3 (CH_2); 129.6 (C-7); 134.3 (C-8); 140.8 (br, C-4); 144.5 (C-5). ^{11}B NMR (64 MHz, CD_2Cl_2, BF_3·Et_2O) δ: 71.3.

Deboration of 4. A 1.7 g amount of the mixture of compounds **4** and **3a,b** obtained in the previous experiment was treated with 3 mL of acetic acid at 0 °C. The reaction mixture was washed with water, and then the organic residue was distilled in vacuum to give 0.6 g of **2-(*E*-pentenyl)-3-norcarene (9)**, yield 58%, n^{20}_D 1.4914, HRMS (*m*/*e*), M$^+$: 162.14174; calcd for $C_{12}H_{18}$ 162.14076. IR (cm^{-1}) ν: 1640, 1660 (C═C); 3025 (C═C—*C*—*H*); 3072 (cyclopropane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.30 (dt, 1H, ^2J = −4.3 Hz, ^3J = 5.1 Hz); 0.45 (dt, ^2J = −4.3 Hz, ^3J = 8.3 Hz); 0.90 (t, 3H); 1.08 (m, 2H); 1.43 (tq, 2H); 2.00 (dt, 2H); 2.22 (dm 1H, ^2J = −15.4 Hz); 2.36 (dm, 1H, ^2J = −15.4 Hz); 3.05 (m, 1H); 5.29 (dm, 1H, ^3J = 10.4 Hz); 5.35−5.60 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 4.2 (CH_2 of cyclopropane); 9.2 and 15.2 (2CH of cyclopropane); 13.60 (CH_3); 22.7 (CH_2); 23.6 (CH_2 of cyclohexene); 34.6 (CH_2); 35.9 (CH); 122.9, 127.3, 129.1, 133.8 (4CH).

Oxidation of the Mixture of Compounds 1, 2, and 3a,b. A 1 mL volume of triethylamine was added dropwise to a solution of 1.54 g of the mixture of compounds **1**, **2**, and **3a,b** in ether at −10 °C. Then carefully at a temperature below 0 °C, 3.26 mL of 30% H_2O_2 was added. The mixture was stirred at 0 °C and then was stored overnight at room temperature. Then it was washed with a small amount of water, and the organic layer was dried with $MgSO_4$. The solvent was removed in vacuum, and the residue was chromatographed on silica gel (eluent hexane−ether 5:3). Five fractions were isolated:

(1) 5-(1-Hydroxybutyl)cycloocta-1,3,6-triene (6): 0.11 g (mixture of two diastereomers in a 4:3 ratio). ^{1}H NMR (200 MHz, $CDCl_3$,) δ: 0.89 (t, 3H, CH_3); 1.40 (m, 4H, 2CH_2); 2.23 (br s, 1H, OH); 2.71 (m, 2H, H-8, H-8a), 3.28 (m, 1H, H-5); 3.50 (m, 1H, C*H*OH); 5.42 (m, 2H, H-1, H-4); 5.72 (m, 3H, H-6, H-3, H-7); 6.23 (m, 1H, H-2). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 14.0 (CH_3); 18.8 and 18.9 (CH_2); 28.0 and 28.2 (CH_2); 36.9 and 37.1 (CH_2); 43.3 and 43.6 (CH); 73.9 and 74.4 (CHOH); 125.3 and 125.8, 126.9 and 127.0, 127.4 and 127.6, 128.3 and 128.7, 129.2 and 129.3 (6 CH). HRMS (*m*/*e*), M$^+$: 178.13528; calcd for $C_{12}H_{18}O$ 178.13567.

(2) *exo*-1-Hydroxy-4,9-dihydro-1*H*-indene (14a): 0.06 g. ^{1}H NMR (200 MHz, $CDCl_3$,) δ: 1.48 (d, 1H, OH, ^3J = 8.3 Hz); 2.97 (dddd, 1H, H-4, ^3J = 11.5, 6.7, 5.4 Hz, ^4J = 1.3 Hz); 3.53 (dm, 1H, H-9, ^3J = 11.5 Hz); 4.68 (t, 1H, H-1, ^3J = 6.8 Hz); 5.57 (ddt, 1H, H-2, ^3J = 10.8, 3.0 Hz, ^4J = 0.9 Hz); 5.73 (m, 1H, H-3); 5.79 (m, 1H, H-5); 6.10 (m, 3H, H-6, H-7, H-8). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 40.3; 42.9; 70.2; 120.3; 123.5; 124.9; 125.9; 133.9; 136.9. HRMS (*m*/*e*), M$^+$: 134.07347; calcd for $C_9H_{10}O$ 134.07311.

(3) *endo*-1-Hydroxy-4,9-dihydro-1*H*-indene (14b): 0.05 g. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.15 (br.s, 1H, OH); 2.86 (ddd, 1H, H-9, ^3J = 11.4, 4.0, 2.6 Hz); 3.75 (dm, ^3J = 11.4 Hz); 4.76 (m, 1H, H-1 ^3J = 1.2 Hz); 5.55 (m, 1H, H-5); 5.73 (m, 1H, H-6); 5.80 (m, 2H, H-7, H-8); 5.89 (dd, 1H, H-3, ^3J = 5.7, 2.4 Hz); 5.98 (dt, 1H, H-2, ^3J = 5.7, 2.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 43.0; 46.4; 85.8; 120.9; 121.3; 125.6; 127.2; 133.3; 135.7. HRMS (*m*/*e*), M$^+$: 134.07295; calcd for $C_9H_{10}O$ 134.07311.

(4) 4-(1-Hydroxybutyl)cycloocta-2,6-dien-1-one (13): 0.30 g (mixture of two diastereomers in a 4:3 ratio). IR (cm^{-1}) ν: 1655, 1670, 1680, 1715, 1730 (C═C, C═O); 3025 (C═C—*C*—*H*); 3480 (OH). ^{1}H NMR (400 MHz, $CDCl_3$,) δ: (major isomer) 0.89 (t, 3H, CH_3); 1.40 (m, 4H, 2CH_2); 1.99 (ddd, 1H, H-5, ^2J = −18.3 Hz, ^2J = 13.3, 6.3 Hz); 2.68 (dt, 1H, H-5a, ^2J = −18.3 Hz, ^3J = 2.9 Hz); 2.97 (m, 1H, H-8); 3.21 (m, 1H, H-4); 3.50 (dt, 1H, C*H*OH, ^3J = 6.6, 2.4 Hz); 3.70 (dd, 1H, H-8a, ^2J = −13.8 Hz, ^3J = 7.9 Hz); 5.50 (m, 1H, H-6); 5.62 (m, 1H, H-7); 5.96 (dm, 1H, H-2, ^3J = 12.5 Hz); 6.15 (dd, 1H H-3, ^3J = 12.5, 8.1 Hz); (minor isomer) 0.89 (t, 3H, CH_3); 1.40 (m, 4H, 2CH_2); 2.28 (ddd, 1H, H-5, ^2J = −17.9 Hz, ^3J = 13.0, 5.7 Hz); 2.38 (dt, 1H, H-5a, ^2J = −17.9 Hz, ^3J = 2.9 Hz); 2.97 (m, 1H, H-8); 3.30 (m, 1H, H-4); 3.61 (dt, 1H, C*H*OH, ^3J = 8.0, 3.6 Hz); 3.68 (dd, 1H, H-8a, ^2J = −14.2 Hz, ^3J = 6.7 Hz); 5.50 (m, 1H, H-6); 5.62 (m, 1H, H-7); 6.01 (dm, 1H, H-2, ^3J = 12.5 Hz); 6.42 (dd, 1H H-3, ^3J = 12.5, 8.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 13.9 (CH_3); 18.9 (CH_2); 29.2 and 31.3 (C-5); 37.3 and 37.6 (CH_2); 44.2 and 45.3 (C-4); 45.1 (C-8); 74.1 and 74.3 (*C*HOH); 120.7 and 120.9 (C-6); 130.3 and 130.9 (C-7); 131.0 and 131.4 (C-2); 143.0 and 143.6 (C-3); 201.9 and 202.2 (C-1). HRMS (*m*/*e*), M$^+$: 194.13042; calcd for $C_{12}H_{18}O_3$ 194.1358.

(5) 1-Hydroxy-6-(1-hydroxybutyl)cycloocta-2,4,7-triene (5): 0.23 g (mixture of two diastereomers in a 4:3 ratio). ^{1}H NMR (200 MHz, $CDCl_3$,) δ: 0.89 (t, 3H, CH_3); 1.40 (m, 4H, 2CH_2); 2.32 (br.s, 1H, OH); 2.96 (br s, 1H, OH); 3.26 (m, 1H, H-4); 3.60 (m, 1H, CHOH); 5.33 (m, 1H, H-1); 5.5−6.0 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 14.0 (CH_3); 18.7 and 18.8 (CH_2); 37.0 (CH_2); 44.5 and 44.9 (C-4); 67.9 (C-1); 73.4 and 73.5 (CHOH); 124.8 and 125.2, 126.2 and 127.0, 127.3 and 128.1, 130.0 and 130.3, 133.3 and 134.1, 137.1 and 137.6 (6 CH). HRMS (*m*/*e*), M$^+$ − H_2: 194.11312; calcd for $C_{12}H_{18}O_2$ − H_2 194.11494.

Methanolysis of the Mixture of Compounds 1, 2, and 3a,b. A 1.2 g amount of the mixture was dissolved in 5 mL of methanol and stored overnight. According to ^{1}H, ^{13}C, and ^{11}B NMR spectra the reaction mixture contained boronic ester **16** and some amount of dihydroindene (compound **2** remained unchanged). After oxidation with basic hydrogen peroxide the organic layer was separated, dried, and evaporated. The residue was distilled in vacuum (in another experiment less pure sample was isolated by chromatography) to give 0.4 g of **8-(1-hydroxybutyl)bicyclo[5.1.0]octa-2,5-diene (7)** yield

49%, bp 56−58 °C (2 mmHg). IR (cm^{-1}) ν: 1620, 1670, 1720 (C═C); 3015 (C═C−*C*−*H*); 3070 (cyclopropane). ^{1}H NMR (400 MHz, $CDCl_3$, 10 mol % Eu(fod)$_3$) δ: 1.79 (t, 3H, CH_3); 3.00 (dt, 1H, H-1, ^3J = 10.3, 8.1 Hz); 3.14 (dt, 1H, H-4, ^2J = −20.5 Hz, ^3J = 7.0 Hz); 3.41 (.m, 1H, H-7); 3.70 (d, 1H, H-4a, ^2J = −20.5 Hz); 4.15 (m, 2H, CH_2); 4.94 (dt, 1H, H-8, ^3J = 9.0, 8.1 Hz); 5.20 (m, 1H of CH_2); 5.82 (m, 1H of CH_2); 6.22 (ddd, 1H, H-5, 11.1, 7.0, ^4J = 2.0 Hz); 6.40 (ddd, 1H, H-2, ^3J = 11.2, 10.3, ^4J = 2.7 Hz); 6.95 (ddd, 1H, H-3, ^3J =11.2, 3.4 Hz); 8.09 (d, 1H, H-6, ^3J = 11.1 Hz); 9.87 (br s, 1H, C*H*OH). ^{13}C NMR (100 MHz, $CDCl_3$ 10 mol % Eu(fod)$_3$) δ: 16.2 (CH_3); 22.9 (CH_2); 25.2 (C-1); 27.1 (C-7); 31.8 (C-4); 35.7 (C-8); 46.9 (CH_2); 84.7 (CHOH); 126.3, 126.6, 129.3, 130.5 (4 CH). HRMS (*m*/*e*), M^+: 178.13451; calcd for $C_{12}H_{18}O$ 178.13567.

Reaction of the Mixture of Compounds 1, 2, and 3a,b with Deuteroacetone and Acetone. A 0.8 g amount of the mixture of compounds **1**, **2**, and **3a,b** was treated with 1 mL of acetone-d_6. ^{1}H, ^{13}C, and ^{11}B NMR spectra taken immediately showed only presence of **21**-d_6 with small admixture of corresponding substituted dihydroindenes formed from **3a,b**. The reaction mixture was stored for 3 h at room temperature, and then it was oxidized with basic H_2O_2. Chromatography on silica gel afforded 0.3 g (32%) of diol **8**-d_6; HRMS (*m*/*e*), $M^+ - H_2O$: 224.20566; calcd for $C_{15}H_{16}D_6O_2 - H_2O$: 224.20463. Similarly an experiment with nondeuterated acetone gave **1-hydroxy-4-(1(*E*)-pentenyl)-7-(2-hydroxypropyl)cyclohepta-2,5-diene (8)**, yield 55%. IR (cm^{-1}) ν: 1590; 1640; 1710 (C═C); 3030 (C═C−*C*−*H*); 3380 (OH). ^{1}H NMR (400 MHz, C_6D_6) δ: 0.92 (t, 3H, CH_3); 1.28 (s, 3H, CH_3); 1.39 (m, 2H, CH_2); 1.40 (s, 3H, CH_3); 2.01 (dt, 2H, CH_2); 2.60 (ddd, 1H, H-7, ^3J = 5.8, 3.6, 2.6 Hz); 3.1 (br s, 1H, OH); 3.75 (m, 1H, H-4); 4.63 (m, 1H, H-1); 5.57 (strongly coupled AB system, 2H, H-2, H-3); 5.68 (ddd, 1H, CH═ from butenyl, ^3J = 15.1, 7.5, 2.5 Hz); 5.72 (dd, 1H, CH═ from butenyl, ^3J = 15.1, 2.3 Hz); 5.92 (strongly coupled AB system, 2H, H-5, H-6. ^{13}C NMR (100 MHz, $CDCl_3$)) δ: 13.5 (CH_3); 22.4 (CH_2); 28.4 and 28.8 (2 CH_3); 34.4 (CH_2); 40.9 (C-4); 50.5 (C-7); 66.8 (C-1); 73.9 (C tert.); 127.6 (C-6); 129.9 (CH═ from butenyl); 131.1 (C-3); 132.7 (CH═ from butenyl); 136.4 (C-2); 138.3 (C-5). HRMS (*m*/*e*), $M^+ - H_2O$: 218.16751; calcd for $C_{15}H_{24}O_2 - H_2O$: 218.16706.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **5**, **6**, **7**, **13**, **14a,b**, **8**, and **9** (15 pages). This material is contained in the libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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