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Pyrolysis of Bicyclo[*n*.2.2] Bridgehead Acetates with a Bridgehead Double Bond

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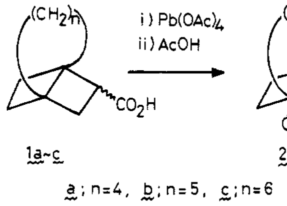
Pyrolysis of bicyclo[*n*.2.2] bridgehead acetates **2a–c** (*n* = 4–6) with a bridgehead double bond has been undertaken with a view to synthesizing bicyclo[*n*.2.2] bridgehead dienes by elimination of acetic acid. It is proved that bicyclo[6.2.2] bridgehead dienes **3** and **4** can be synthesized successfully by the pyrolysis of **2c**. The symmetric bridgehead diene **3**, which is a dihydro derivative of [6]paracyclophane, shows remarkable properties due to the presence of two distorted double bonds in close proximity. In the case of bicyclo[5.2.2] system **2b**, pyrolysis gives 2,8-dimethylenebicyclo[5.2.0]nonane (**10**) as a sole product probably derived from [3,3] sigmatropic rearrangement of unstable bridgehead diene intermediate **12**. Moreover, in the case of bicyclo[4.2.2] system **2a**, pyrolysis affords trienes **13** and **14** as the major products which are formed by retro-ene reaction of **2a** followed by elimination of acetic acid rather than through bicyclo[4.2.2] bridgehead diene intermediates such as **17** and **18**, presumably because of the strain inherent in bicyclo[4.2.2]dec-1(8)-ene skeleton.

The chemistry of bridgehead alkenes has been of special interest for many years with regard to the stability, chemical reactivity, and physical properties associated with the distortion imposed on the double bond.[1] Many bridgehead olefins having short bridges have been synthesized and isolated or detected as unstable intermediates owing to the development of new efficient methods for introduction of bridgehead double bonds. Recent efforts have been focused on the synthesis of more strained bicyclic molecules having two bridgehead double bonds, i.e., bridgehead dienes.[1e,2] It is anticipated to be very difficult to isolate and characterize the bridgehead dienes with short bridges not only in the thermodynamic sense (i.e., difficulty in introduction of two strained double bonds at each bridgehead position in a molecule) but also because of kinetic instability (i.e., facility of skeletal change by sigmatropic rearrangements even under mild conditions[2c–g] due to the presence of two distorted double bonds in close proximity).

As part of the study on synthesis of important polycarbocyclic systems from readily accessible [*n*.3.2]propellanones, we have recently developed an efficient route to bicyclo[*n*.2.2] bridgehead alkenes **2a–c** (*n* = 4–6) having an acetoxyl group at the opposite bridgehead position by the oxidative decarboxylation of [*n*.2.2]propellane carboxylic acids **1a–c** by lead tetraacetate.[3] Since elimination of acetic acid by vapor-phase pyrolysis of bridgehead acetates has been shown to be a useful method for preparation of bridgehead alkenes,[2f,4] it may be possible to introduce another bridgehead double bond in the bicyclo[*n*.2.2] skeleton by pyrolysis of the bridgehead acetates **2a–c**. It should be noted, however, that a 1,3-diene and two types of 1,4-dienes may be formed in principle depending on the position of hydrogen eliminated (Scheme I). From the above points of view, we report here on the results of pyrolysis of **2a–c** and also on the scope and limitation of the bridgehead diene synthesis by the present simple pyrolytic method.[5]



Scheme I

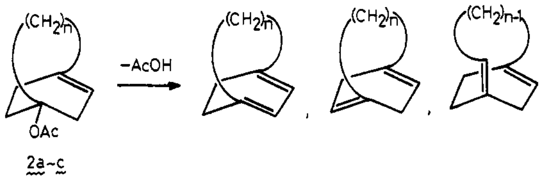


Table I. Product Distribution in Pyrolysis of 2c

temp, °C	conversion, %	products,[a] % 3	4	5
320	20	25	58	9
350	82	19	57	15
400[b]	95	3	30	33

[a] Yields based on the reacted **2c**. [b] A considerable amount of unidentified products were formed.

Pyrolysis of Bicyclo[6.2.2]dodec-1(10)-en-8-yl Acetate (2c). Pyrolysis of **2c** was conducted by passing a hexane solution of **2c** (0.05 M) with a nitrogen flow (10 mL/min) into a Pyrex column packed with Pyrex chips which was heated at 320–420 °C (contact time about 20 s). Products were collected in a cold trap (−78 °C) containing powdered potassium carbonate. Analysis of the products by GLC showed that the product distribution was markedly dependent on the reaction temperature as shown

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(1) For recent reviews: (a) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464. (b) Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41. (c) Keese, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 528. (d) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 117–133. (e) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. (f) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

(2) (a) Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342. (b) Lindner, H. J.; Kitschke, B.; Liesner, M.; Seebach, D. *Helv. Chim. Acta* **1977**, *60*, 1151. (c) Shea, K. J.; Wise, S. *Tetrahedron Lett.* **1978**, 2283. (d) Wiseman, J. R.; Vanderbilt, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 7730. (e) Rastetter, W. H.; Richard, T. J. *Ibid.* **1979**, *101*, 3893. (f) Warner, P.; Boulanger, W. *Tetrahedron Lett.* **1980**, *21*, 123. (g) Wiberg, K. B.; Matturro, M.; Adams, R. *J. Am. Chem. Soc.* **1981**, *103*, 1600. (h) Turkenburg, L. A. M.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1980**, *102*, 3257. (i) See also: Warner, P.; Chang, S.-C.; Powell, D. R.; Jacobson, R. A. *Ibid.* **1980**, *102*, 5125 and references cited therein.

(3) (a) Sakai, Y.; Toyotani, S.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1979**, 3855. (b) Sakai, Y.; Tobe, Y.; Odaira, Y. *Chem. Lett.* **1980**, 691. (c) Sakai, Y.; Toyotani, S.; Ohtani, M.; Matsumoto, M.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1474.

(4) (a) Adams, B. L.; Kovacic, P. *J. Am. Chem. Soc.* **1975**, *97*, 2829. (b) Becker, K. B.; Pfluger, R. W. *Tetrahedron Lett.* **1979**, 3713. (c) Klebach, T. C.; Jones, M., Jr. *Ibid.* **1981**, *22*, 497.

(5) Part of this work has been reported in a preliminary form: Tobe, Y.; Ueda, Y.; Matsumoto, M.; Sakai, Y.; Odaira, Y. *Tetrahedron Lett.* **1982**, *23*, 537.

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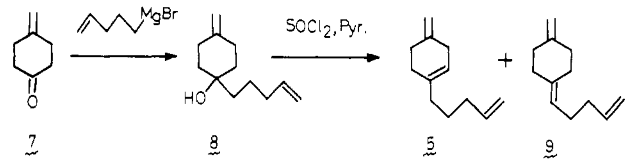
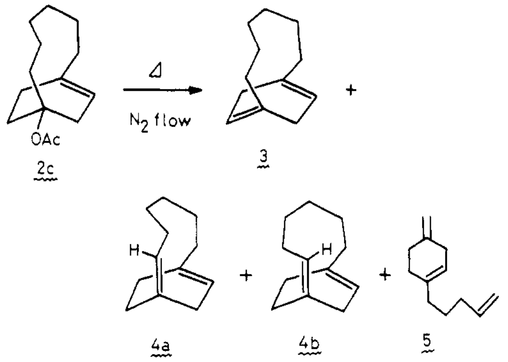
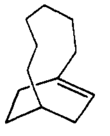
Scheme II



in Table I.[6] At low temperature (320 °C), two products, **3** and **4** (**4a** + **4b**), were formed predominantly, while the ratio of **3** decreased with respect to triene **5** when the reaction temperature was elevated (350 °C). The fact that **5** is a secondary product derived from **3** was confirmed by the independent pyrolysis of **3** under similar conditions. At higher temperature (400 °C), most of **3** was converted to **5**, and many other products (at least three peaks in GLC), presumably derived from **4**, appeared which were major products at temperatures above 450 °C (quartz column).[7]



The structure of the symmetric bridgehead diene **3** was elucidated on the basis of the ^{13}C NMR spectrum which was comprised of six signals [δ 145.3 (s), 126.6 (d), 38.1 (t), 33.0 (t), 29.9 (t), 26.6 (t)], indicating the presence of symmetry. Moreover, in the ^{1}H NMR spectrum, the vinyl proton of **3** appears as a doublet at δ 5.73 (J = 5 Hz), excluding the possibility of a 1,3-diene.[8] Although the unsymmetric diene **4** was homogeneous in GLC, it was deduced that **4** was about a 1:1 mixture of dienes **4a** and **4b** on the following grounds.[9] (i) The ^{13}C NMR spectrum indicates the presence of four quarternary (singlets; δ 147.2, 145.1, 139.3, 138.6) and four tertiary (doublets; δ 133.8, 129.9, 121.4, 121.1) olefinic carbons, (ii) the ^{1}H NMR spectrum shows three kinds of vinyl protons [δ 4.75–5.10 (m, 1 H), 5.78 (br d, J = 8 Hz, 0.5 H), 5.98–6.22 (m, 0.5 H)], and (iii) catalytic hydrogenation of **4** (**4a** + **4b**) over Pd/C gave the bridgehead monoolefin **6**[3c] as a sole product.



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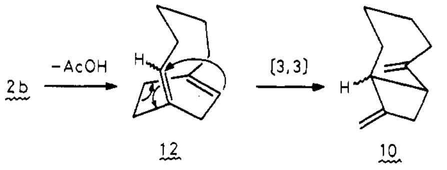
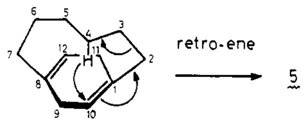
Scheme III



The structure of triene **5** was elucidated on the basis of the ^{1}H NMR spectrum and was confirmed by identity with the authentic sample prepared from 4-methylenecyclohexanone (**7**)[10] as shown in Scheme II.

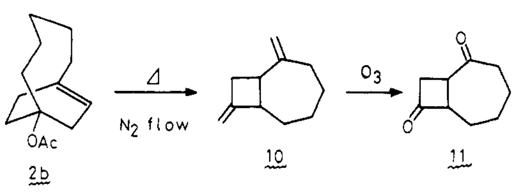
It was thus proved that bicyclo[6.2.2]dodecadienes **3** and **4** having two bridgehead double bonds are synthesized successfully from **2c** by the simple pyrolytic method and that both of dienes **3** and **4** are stable under nitrogen at ambient temperature although they are highly sensitive to oxygen.

It should be noted that **3** is a dihydro derivative of [6]paracyclophane which is the smallest [n]paracyclophane synthesized to date.[11] As expected, **3** shows some unusual properties due to the presence of two distorted double bonds in close proximity. In the UV spectrum, the absorption [λ_{max} (cyclohexane) 205 nm (ε 3800)] extends to 250 nm, and a shoulder appears at 232 nm (ε 830) which must be compared with the spectrum of **6** whose end absorption falls at 220 nm. This long-wavelength absorption of **3** is attributable to the interaction of nonconjugated bridgehead double bonds.[12] In the ^{1}H NMR spectrum, a two-proton multiplet is observed at δ 0.2–0.5 which is assigned to the methylene protons on the hexamethylene bridge (C_4 and C_5) shielded by the bridgehead double bonds. This fact indicates that the methylene protons of the bridge are located over the bridgehead double bonds in close proximity. Therefore, a retro-ene reaction[13] of **3** leading to triene **5**, which involves the shift of H_4 (or H_5) to the tertiary carbon C_{10} (or C_{12}) of the bridgehead double bond, may take place smoothly.



3

Pyrolysis of Bicyclo[5.2.2]undec-1(9)-en-7-yl Acetate (2b). When the pyrolysis of **2b** was carried out as described for **2c** at 320–450 °C, 2,8-dimethylenebicyclo[5.2.0]nonane (**10**) was obtained as a sole product almost quantitatively in every case (conversion 10–80%).[6] The



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[6] Yields of the pyrolysis products are based on the reacted starting materials and are almost quantitative in most cases.

[7] These products, however, were not investigated because of poor separation in GLC.

[8] The vinyl proton of the corresponding bridghead monoolefin **6** appeared as a broad doublet at δ 5.66 (J = 7 Hz).[3c]

[9] Since diene **4a** is composed of *trans*-cyclodecene and *cis,trans*-cyclodeca-1,4-diene and **4b** is composed of *cis*-cyclodecene and *trans, trans*-cyclodeca-1,4-diene, the relative thermodynamic stabilities of **4a** and **4b** seem to be comparable. Cf.: (a) Cope, A. C.; Moore, P. T.; Moore, W. R. *J. Am. Chem. Soc.* **1960**, *82*, 1744. (b) Buemi, G.; Zuccarello, F.; Favini, G. *J. Mol. Struct.* **1974**, *21*, 41. There is a possibility of interconversion between **4a** and **4b** because the isomerization barrier may be smaller than that of *cis*- and *trans*-cyclodecenes in view of the highly distorted double bond of **4a** and **4b**.

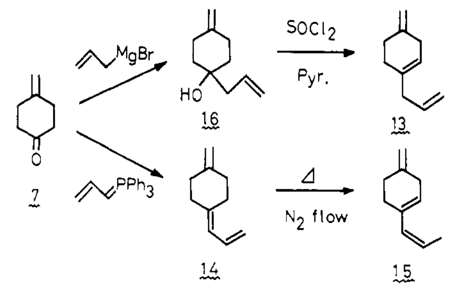
[10] Sonoda, A.; Moritani, I.; Miki, J.; Tsuji, T.; Nishida, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1777.

[11] (a) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (b) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1977**, *99*, 5815. (c) Liebe, J.; Wolff, C.; Tochtermann, W. *Tetrahedron Lett.* **1982**, *23*, 171. (d) Tobe, Y.; Odaira, Y. 4th International Conference on Organic Synthesis, Aug 22–27, 1982, Tokyo; Abstract No. B-I-6101.

[12] For a similar interaction between two bridgehead double bonds: Marshall, J. L.; Hall, L. *Tetrahedron* **1981**, *37*, 1271 and references therein.

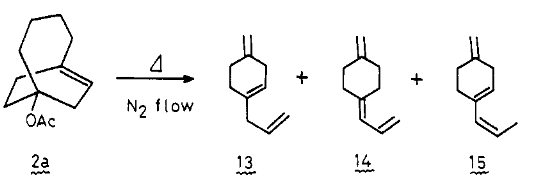
[13] For a retro-ene reaction of a bridgehead olefin, see ref 4b.

Scheme IV

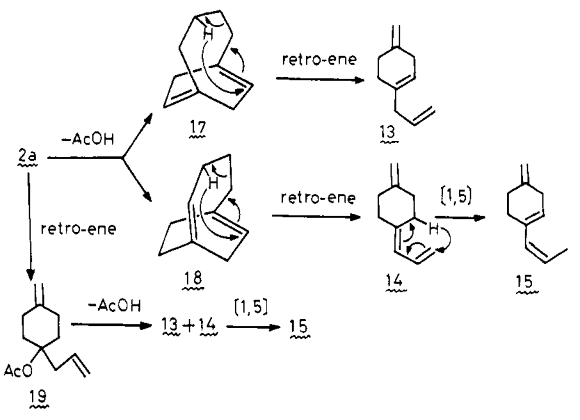


structure elucidation of **10** was based on the spectroscopic data (mainly ^{13}C NMR spectrum) and chemical transformation. The salient features of the ^{13}C NMR spectrum include two quarternary (singlets; δ 152.4, 151.3) and two secondary (triplets; δ 109.5, 105.0) olefinic absorptions and two doublets (δ 48.5, 40.2) due to the bridgehead carbons. Furthermore, the dimethylenebicyclo[5.2.0]nonane skeleton of **10** was elucidated[14] from the fact that the ozonolysis of **10** gives the dione **11** which shows an IR absorption at 1780 cm^{-1}, being characteristic of cyclobutanone. On the mechanistic consideration for the formation of **10**, it is reasonable to consider that **10** is formed by [3,3] sigmatropic rearrangement of an unsymmetric bicyclo[5.2.2] bridgehead diene intermediate (**12**) as shown in Scheme III, though no bicyclo[5.2.2] bridgehead diene including **12** was detected even by pyrolysis at lower temperatures.[15]

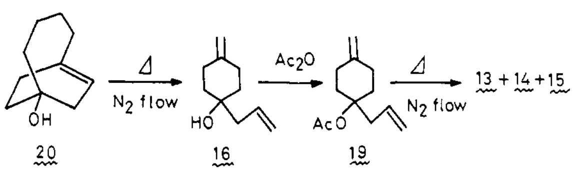
Pyrolysis of Bicyclo[4.2.2]dec-1(8)-en-6-yl Acetate (2a). Pyrolysis of **2a** at 380 °C gave three trienes, 1-allyl-4-methylenecyclohexene (**13**), 1-allylidene-4-methylene cyclohexene (**14**), and 1-propenyl-4-methylenecyclohexene (**15**), in 65%, 5%, and 25% yields, respectively (conversion 20%),[6] although pyrolysis over 400 °C gave a complex mixture of products presumably derived by further degradations of **13–15**. Moreover, reaction at reduced temperatures (330–360 °C) did not give any product except for **13–15**, with a decreasing conversion of **2a**. The structures of **13–15** were determined on the basis of the spectroscopic data, especially ^{1}H NMR spectra. The salient features of the ^{1}H NMR spectra of **13–15** involve broad singlets due to the exo methylene protons at δ 4.63–4.75, an ABX pattern due to the vinyl groups of **13** and **14** (**13**, J_{AB} = 1Hz, J_{AX} = 12 Hz, J_{BX} = 14 Hz; **14**, J_{AB} = 2 Hz, J_{AX} = 11 Hz, J_{BX} = 16 Hz), and a doublet at δ 1.76 (J = 7 Hz) assigned to the allylic methyl group of **15**. The structures of **13** and **14** were confirmed unambigously by identity with the respective authentic samples which were prepared from **7** (Scheme IV). Moreover, from the fact that pyrolysis of **14** with a nitrogen flow at 380 °C gives **15** quantitatively (conversion 80%),[6] it is deduced that **15** is a secondary product derived by the [1,5] sigmatropic hydrogen shift of **14** and, therefore, that the side chain of **15** has the cis configuration.



Scheme V



Scheme VI



In analogy with the case of **5**, the formation of trienes **13** and **14** may be explained in terms of retro-ene reaction[12] via unstable bicyclo[4.2.2] bridgehead diene intermediates **17** and **18** formed by elimination of acetic acid from **2a**. Alternatively, it is conceivable that retro-ene reaction of the strained bridgehead olefin **2a** occurs in place of elimination under the pyrolysis conditions to afford acetate **19**, which furnishes the obtainable trienes **13** and **14** by the subsequent elimination of acetic acid, though **19** could not be detected in pyrolysis of **2a** (Scheme V). In order to determine the mechanistic pathway leading to the formation of **13** and **14**, we undertook the following experiments (Scheme VI). (i) Pyrolysis of alcohol **20**[3c] having bicyclo[4.2.2]dec-1(8)-ene skeleton under usual conditions (380 °C) gave alcohol **16** derived from retro-ene reaction (conversion 16%) as a single product.[6] (ii) Acetate **19**, prepared by acetylation of alcohol **16**, was pyrolyzed at 380 °C to give **13–15** in 59%, 10%, and 31% yields, respectively (conversion 100%).[6] The above results clearly suggest the feasibility of the formation of **13** and **14** by retro-ene reaction of **2a** followed by elimination of acetic acid from **19** rather than the another pathway through the bridgehead dienes **17** and **18**. Consequently, it is deduced that, in the case of **2a**, retro-ene reaction predominates over elimination of acetic acid under the pyrolysis conditions owing to the strain inherent in the bicyclo[4.2.2] bridgehead alkene system.

In summary, highly strained bicyclo[6.2.2] bridgehead dienes **3** and **4** could be readily synthesized from **2c** by elimination of acetic acid by the simple pyrolytic method. In the case of bicyclo[5.2.2] system **2b**, however, although elimination took place efficiently, the posturated bridgehead diene **12** did not survive under the pyrolysis conditions, giving rise to [3,3] sigmatropic rearrangement to afford diene **10** very smoothly. Moreover, in the case of highly strained bicyclo[4.2.2] system **2a**, elimination could not compete with retro-ene reaction owing to the strain inherent in the bicyclo[4.2.2]dec-1(8)-ene skeleton, and, therefore, the bicyclo[4.2.2] bridgehead diene was not

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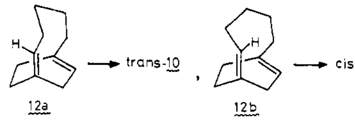
[14] Judging from the ^{13}C NMR spectra, it is apparent that **10** is a single cis or trans isomer, though the stereochemistry is not clear as yet.

[15] It is interesting to note that the exclusive formation of *trans*- or *cis*-**10** indicates the specific formation of either **12a** or **12b** from **2b** since Cope rearrangement of **12a** or **12b** would give *trans*-**10** or *cis*-**10**, respectively. However, we presently have no explanation to offer for this stereospecificity.



formed by the pyrolysis of **2a**.

Experimental Section

IR spectra were recorded on a Hitachi 260-10 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JNM-PS-100 and JEOL JNM-FX-60S spectrometers, respectively. Mass spectra were obtained on a Hitachi RMU-6E instrument. Analytical GLC was carried out on a Hitachi 163 gas chromatograph with 10% FFAP and 5% SE-30 columns, and preparative GLC separation was conducted on a Varian Aerograph 920 chromatograph.

Pyrolysis of 2a–c. General Procedure. Solutions of **2a–c** in hexane (0.05 M) were passed with a nitrogen flow (10 mL/min) through a vertical Pyrex column packed with Pyrex chips which was heated at 320–420 °C (contact time about 20 s). Pyrolysis at 450 °C was conducted with a quartz column. Products were collected in a cold trap (-78 °C) containing powdered potassium carbonate. After being filtered, the solvent was evaporated in vacuo. The products were analyzed by GLC and were separated by quick chromatography on silica gel (Fuji-Davison No. 922 silica gel) followed by preparative GLC.

Pyrolysis of 2c. Pyrolysis of **2c** at 320–380 °C gave the bridgehead dienes **3** and **4** (**4a** + **4b**) and the triene **5** as the major products. Pyrolysis over 400 °C gave considerable amount of unidentified products. Pyrolysis of the isolated sample of **3** under similar conditions afforded **5** quantitatively.

3: IR (CCl$_4$) 3040, 1625, 875 cm^{-1}; MS, *m/e* (relative intensity) 162 (M$^+$, 24), 106 (58), 105 (52), 91 (100), 79 (78); ^{1}H NMR (CDCl$_3$) δ 0.20–0.52 (m, 2 H), 0.70–2.80 (m, 14 H), 5.73 (br d, J = 5 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 145.3 (s), 126.6 (d), 38.1 (t), 33.0 (t), 29.9 (t), 26.6 (t); UV (cyclohexane) 205 nm (ϵ 3780), 232 (sh, 826). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.53; H, 10.86.

4 (4a +4b): IR (CCl$_4$) 3010, 1650, 1620, 875 cm^{-1}; MS, *m/e* (relative intensity) 162 (M$^+$, 85), 119 (82), 101 (100), 93 (74), 79 (73); ^{1}H NMR (CDCl$_3$) δ 0.65–2.90 (m, 16 H), 4.75–5.10 (m, 1 H), 5.78 (br d, J = 8 Hz, 0.5 H), 5.98–6.22 (m, 0.5 H); ^{13}C NMR (CDCl$_3$) δ 147.2 (s), 145.1 (s), 139.3 (s), 138.6 (s), 133.8 (d), 129.9 (d), 121.4 (d), 121.1 (d), 37.8 (t), 36.1 (t), 34.0 (t), 31.4, 30.8, 29.6, 29.3, 26.4, 25.0, 24.4, 23.2, 20.6 (t); UV (cyclohexane) 202 nm (ϵ 6540), 216 (sh, 5480). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.46; H, 11.03.

5: IR (CCl$_4$) 3070, 1660, 1650, 1640, 990, 905, 880, 860 cm^{-1}; MS, *m/e* (relative intensity) 162 (M$^+$, 31), 118 (33), 105 (100), 93 (56), 91 (55), 79 (37); ^{1}H NMR (CCl$_4$) δ 1.50 (tt, 2 H), 1.82–2.42 (m, 8 H), 2.62–2.84 (m, 2 H), 4.72 (br s, 2 H), 4.94, 4.97 (2 ddd, J_{AB} = 1 Hz, J_{AX} = 9 Hz, J_{BX} = 17 Hz, 2 H), 5.26–5.44 (m, 1 H), 5.58–6.06 (m, 1 H). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.81; H, 11.32.

Pyrolysis of 2b. Pyrolysis of **2b** at 320–450 °C gave the diene **10** as a sole product (conversion 10–80%): IR (CCl$_4$) 3070, 1670, 1635, 870 cm^{-1}; MS, *m/e* (relative intensity) 148 (M$^+$, 8), 133 (50), 105 (73), 91 (100), 79 (68); ^{1}H NMR (CDCl$_3$) δ 1.10–2.00 (m, 7 H), 2.30–3.20 (m, 5 H), 4.60–5.95 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 152.4 (s), 151.3 (s), 109.5 (t), 105.0 (t), 48.5 (d), 40.2 (d), 37.6 (t), 32.5 (t), 31.7 (t), 31.5 (t), 29.1 (t). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.81; H, 10.65.

Pyrolysis of 2a. Pyrolysis of **2a** below 380 °C gave the trienes **13–15** as the major products. Pyrolysis over 400 °C gave complex mixtures of products.

13: IR (CCl$_4$) 3070, 1675, 1650, 1640, 915, 890 cm^{-1}; MS, *m/e* (relative intensity) 134 (M$^+$, 16), 93 (100), 91 (75), 77 (48); ^{1}H NMR (CDCl$_3$) δ 1.90–2.18 (m, 2 H), 2.24 (br d, J = 5 Hz, 2 H), 2.58–2.82 (m, 4 H), 4.72 (br s, 2 H), 4.98, 5.00 (2 ddd, J_{AB} = 1 Hz, J_{AX} = 12 Hz, J_{BX} = 14 Hz, 2H), 5.30–5.46 (m, 1 H), 5.54–6.02 (m, 1 H). Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.36; H, 10.61.

14: IR (CCl$_4$) 3070, 1650, 1635, 910, 885 cm^{-1}; MS, *m/e* (relative intensity) 134 (M$^+$, 100), 119 (52), 93 (61), 91 (76), 79 (54), 77 (49); ^{1}H NMR (CCl$_4$) δ 2.05–2.50 (m, 8 H), 4.63 (br s, 2 H), 4.93, 5.05 (2 ddd, J_{AB} = 2 Hz, J_{AX} = 10 Hz, J_{BX} = 16 Hz, 2 H), 5.78 (d, J = 11 Hz, 1 H), 6.52 (ddd, J = 10, 11, 16 Hz, 1 H). Anal. Calcd for $C_{10}\ H_{14}$: C, 89.49; H, 10.51. Found: C, 89.35; H, 10.62.

15: IR (CCl$_4$) 3070, 3010, 1655, 890 cm^{-1}; MS, *m/e* (relative intensity) 134 (M$^+$, 79), 119 (57), 91 (100); ^{1}H NMR (CDCl$_3$) δ 1.76 (d, J = 7 Hz, 3 H), 2.30 (br s, 4 H), 2.77–2.97 (m, 2 H), 4.75 (br s, 2 H), 5.19–5.90 (m, 3 H). Anal. Calcd for $C_{10}H_{14}$: C, 84.49; H, 10.51. Found: C, 89.23; H, 10.42.

Preparation of Authentic Sample of 5. A solution of 520 mg (4.73 mmol) of 4-methylenecyclohexanone (**7**)[9] in 5 mL of ether was added to a solution of pentenylmagnesium bromide prepared from 1.19 (8.0 mmol) of 5-bromopent-1-ene[16] and 194 mg of (8.0 mmol) of magnesium in 5 mL of ether, and the mixture was refluxed for 2 h. Water was added followed by 10% HCl, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined extract was washed with 5% NaHCO$_3$ and water. After the mixture was dried (MgSO$_4$), the solvent was evaporated, and the residue was chromatographed on silica gel. Elution with 10% ether–petroleum ether gave 330 mg (39%) of the alcohol **8**: IR (neat) 3500, 3060, 1645, 1125, 1100, 950, 880 cm^{-1}; MS, *m/e* (relative intensity) 180 (M$^+$, not detected), 162 (55), 107 (55), 105 (100), 93 (89), 91 (67), 79 (61); ^{1}H NMR (CCl$_4$) δ 1.10 (br s, 1 H), 1.30–1.80 (m, 8 H), 1.80–2.50 (m, 6 H), 4.53 (br s, 2 H), 4.88, 4.92 (2 ddd, J_{AB} = 1 Hz, J_{AX} = 10 Hz, J_{BX} = 17 Hz, 2 H), 5.52–6.00 (m, 1 H). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.90; H, 10.89.

Thionyl chloride (0.1 mL) was added dropwise to a solution of 53 mg (0.29 mmol) of **8** in 1 mL of pyridine at 0 °C, and the solution was stirred at room temperature for 30 min. The mixture was poured into water and extracted with ether. The extract was washed with 10% HCl, 5% NaHCO$_3$, and water and then dried (MgSO$_4$). Evaporation of the solvent gave 46 mg (97%) of pale yellow oil containing the trienes **5** and **9** (4:1) which were separated by preparative GLC.

9: IR (CCl$_4$) 3070, 1640, 1035, 970, 905, 880, 855 cm^{-1}; MS, *m/e* (relative intensity) 162 (M$^+$, 55), 107 (49), 105 (100), 93 (79), 91 (72), 79 (60); ^{1}H NMR (CCl$_4$) δ 2.00–2.34 (m, 12 H), 4.58 (br s, 2 H), 4.92, 4.96 (2 ddd, J_{AB} = 1 Hz, J_{AX} = 10 Hz, J_{BX} = 18 Hz, 2 H), 5.12 (t, J = 6 Hz, 1 H), 5.52–5.98 (m, 1 H). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.61; H, 11.12.

Ozonolysis of 10. Ozone was bubbled for 30 min into a solution of 108 mg (0.73 mmol) of **10** in 5 mL of ethyl acetate cooled to -70 °C. After being warmed to room temperature, a small amount of 10% Pd/C was added, and the mixture was stirred under atmospheric hydrogen for 3 h. The catalyst was filtered off, and the filtrate evaporated. Preparative GLC gave 58 mg (52%) of the dione **11**: IR (neat) 1780, 1700, 1120 cm^{-1}; MS, *m/e* (relative intensity) 152 (M$^+$, 16), 124 (82), 81 (64), 80 (100), 67 (63); ^{1}H NMR (CCl$_4$) δ 1.05–2.20 (m, 6 H), 2.40–3.80 (m, 6 H); disemicarbazone, mp 250–253 °C dec. Anal. Calcd for $C_{11}H_{18}O_2N_6$: C, 49.61; H, 6.81; N, 31.56. Found: C, 49.31; H, 6.72; N, 31.39.

Preparation of Authentic Sample of 13. The reaction of **7** (420 mg, 3.82 mmol) with allylmagnesium bromide prepared from 1.21 g (10 mmol) of allyl bromide and 243 mg (10 mmol) of magnesium as described for the preparation of **8** gave 192 mg (33%) of the alcohol **16** after chromatography on silica gel: IR (neat) 3400, 3070, 1650, 1645, 1105, 950, 915, 890 cm^{-1}; MS, *m/e* (relative intensity) 152 (M$^+$, 1), 134 (7), 111 (100), 93 (51); ^{1}H NMR (CCl$_4$) δ 1.10–1.75 (m, 5 H), 1.86–2.55 (m, 6 H), 4.52 (br s, 2 H), 5.04, 5.08 (2 ddd, J_{AB} = 2 Hz, J_{AX} = 10 Hz, J_{BX} = 19 Hz, 2 H), 5.56–6.08 (m, 1 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.67; H, 10.73.

Dehydration of 197 mg (1.30 mmol) of **16** as described for that of **8** gave 81 mg (46%) of **13** as a sole product which was identical (IR, ^{1}H NMR, and GLC) with the sample obtained by the pyrolysis of **2a**.

Preparation of Authentic Sample of 14. Allyltriphenylphosphonium bromide[17] (4.0 g, 10.4 mmol) in 20 mL of Me$_2$SO was added dropwise to a solution of methylsulfinyl carbanion prepared from 504 mg of 50% sodium hydride (10.5 mmol) and 6 mL of Me$_2$SO, and the resulting solution was stirred at room temperature for 30 min. A solution of 1.13 g (10.3 mmol) of **7** in 10 mL of Me$_2$SO was added dropwise, and the mixture was heated at 50 °C for 1 h. After careful addition of water, the precipitates were filtered off and washed with petroleum ether. The filtrate was extracted with petroleum ether, and the combined organic layer was washed with water and dried (MgSO$_4$). The solvent was evaporated, and the residue was chromatographed

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on silica gel with petroleum ether as eluent to afford 510 mg (41%) of **14** which was identical (IR, ^{1}H NMR, and GLC) with the sample obtained by the pyrolysis of **2a**.

Pyrolysis of 14. Pyrolysis of **14** under usual conditions at 380 °C gave a mixture of **14** and **15** in a ratio of 1:4.

Preparation of 19. A solution of 239 mg (2.34 mmol) of acetic anhydride in 1 mL of dichloromethane was added dropwise to a solution of 178 mg (1.17 mmol) of **16** and 319 mg (2.34 mmol) of 4-(dimethylamino)pyridine(18) in 3 mL of the same solvent, and the mixture was stirred at room temperature for 12 h. The solution was diluted with ether and washed with 5% HCl, 5% $NaHCO_3$, and water. After being dried ($MgSO_4$), the solvent was evaporated to give 224 mg (99%) of the acetate **19**: IR (neat) 3070, 1735, 1645, 1245, 1020, 950, 915, 885 cm^{-1}; MS, *m/e* (relative intensity) 194 (M^+, not detected), 153 (16), 134 (39), 111 (78), 93 (100); ^{1}H NMR (CCl_4) δ 1.19–1.65 (m, 2 H), 1.92 (s, 3 H), 2.00–2.44 (m, 6 H), 2.59 (d, J = 8 Hz, 2 H), 4.55 (br s, 2 H), 4.84–5.18 (m, 2 H), 5.44–5.92 (m, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.04; H, 9.52.

Pyrolysis of 19. Pyrolysis of **19** under usual conditions at 380 °C gave a mixture of **13**–**15** quantitatively in a ratio of about 6:1:3.

Pyrolysis of 20. Pyrolysis of **20**(3c) was carried out at 380 °C to afford a mixture of unreacted **20** (conversion 16%) and the alcohol **16** which was identical (IR, ^{1}H NMR, and GLC) with the sample prepared from **7**.

Registry No. 2a, 73626-91-2; **2b**, 73626-92-3; **2c**, 73648-76-7; **3**, 82353-64-8; **4a**, 82353-65-9; **4b**, 82353-66-0; **5**, 82353-67-1; **7**, 29648-66-6; **8**, 84215-13-4; **9**, 84215-14-5; **10**, 84215-15-6; **11**, 84215-16-7; **11** disemicarbazone, 84215-17-8; **13**, 84215-18-9; **14**, 84215-19-0; **15**, 84237-45-6; **16**, 84215-20-3; **19**, 84215-21-4; **20**, 77871-16-0; 5-bromo-1-pentene, 1119-51-3; allyl bromide, 106-95-6; triphenyl(2-propenylidene)phosphorane, 15935-94-1.

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Stereoselectivity in Organoborane Rearrangement: Relationship to the Mechanism of Hydroboration

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Hydroboration of 1,2-dimethylcyclohexene and subsequent rearrangement of the tertiary to the primary alkylborane occur with substantial (≥99:1) suprafacial selectivity. Similar though less pronounced behavior is found for the rearrangement of the tertiary to the secondary alkylborane. These results rule out, as the lowest energy pathway, dissociation (dehydroboration) to the free olefins followed by readdition with reversed regiochemistry, since hydroborations of these olefins exhibit little selectivity. The observed stereoselectivity provides strong support for an intramolecular process, most likely involving an intermediate π complex, which must give rearranged alkylborane faster than dissociated entities. Similar stereochemical results are obtained for the rearrangement in the presence or absence of THF, showing that solvent plays no critical role in the intramolecular migration. As a further mechanistic probe, B_2D_6 was employed, and the deuterium content was examined in various products. Evidence for an exchange process at the tertiary center β to boron was found. In general, the results are compatible with the proposed π-complex mechanism. An unusual feature is the incorporation of deuterium at the borane migration terminus, for which a free-radical mechanism is suggested. The rearrangement results are considered in the context of the mechanism of hydroboration. Although a π-complex intermediate has been suggested for hydroboration, it is concluded that such an intermediate (if it exists) must be fundamentally different from that involved in the rearrangement. This conclusion is surprising considering the close similarities of the two processes.

The mechanisms of hydroboration and of organoborane rearrangement are thought to be closely related, in that the latter can be viewed as a sequence of elimination (dehydroboration) followed by readdition reactions with the opposite regiochemistry.(1) The rearrangement process has recently been shown by Brown and co-workers(2) to be greatly speeded by bulky substituents on boron, with concurrent improvement in product selectivity for a series of reactions starting with 3-hexene. In earlier work Brown demonstrated that the thermal isomerization of boranes leads to migration to the least substituted carbon; in simple acyclic examples 90–99% primary alcohols result from subsequent alkaline peroxide oxidation.(3) Methylcyclohexenes show a similar but less pronounced preference for rearrangement to cyclohexylmethylborane, with 50–60% primary product being formed. The latter rearrangements were found to be relatively slow, presumably due to the required formation of the unfavorable tertiary alkylborane as an intermediate.(4) All these observations were readily explained by a dehydroboration–readdition mechanism in which free olefin intermediate is formed.(3) Further support of this gross mechanistic feature is found in the olefin exchange process whereby heating a mixture of high-boiling alkene and organoborane derived from a more volatile alkene allows the isolation of lower boiling olefin by distillation.(5) Similar conclusions have been drawn by Midland(6) in a recent study using *B*-alkyl 9-BBN derivatives.

The detailed mechanism of the very important hydroboration reaction continues to be a matter of interest and considerable speculation. The net stereochemistry of the reaction appears to be generalizable as involving either

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