Intramolecular Addition *versus* Novel Carbon–Hydrogen Bond Insertion Reactions of *n*-Alkenyl-Substituted Cyclopropylidenes†

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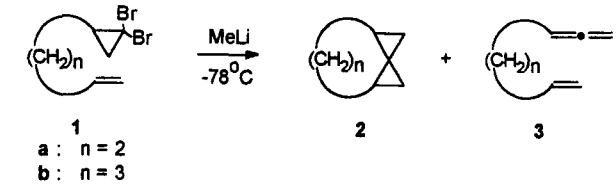
Introduction

Inter- and intramolecular addition reactions of cyclopropylidenes (or the related carbenoids) have successfully been employed for efficient construction of strained spiropentanes.[1] Skattebøl[2] reported about 30 years ago on the reactive behavior of 2-(3-butenyl)-1,1-dibromocyclopropane (**1a**) (n = 2). The divalent carbon generated from **1a** reacts either by addition to the double bond to form **2a** or by a cyclopropylidene allene rearrangement to give **3a**.[2,3] Both reactions are temperature dependent.[2,3] At −78 °C the formation of spiropentane **2a** and allene **3a** proceeds to about the same extent (48:52), while at higher temperatures allene formation dominates.[2,3] This intramolecular carbene addition reaction has repeatedly been used for the construction of the tricyclo[4.1.0.0^{1,3}]heptane carbon skeleton.[4]

For intramolecular addition reactions of cyclopropylidenes, the length of the carbon chain separating the cyclopropylidene ring and the double bond seems to be of prime importance. Apparently, the outcome of the reaction is sensitive to the distance between the carbene carbon and the double bond (see Figure 1). For n = 3, at −78 °C the addition reaction has been reported to be almost negligible (**2b**/**3b** = 90:10),[2,3] while for n = 4 only allene formation was observed.[3]

The reaction of **1b** with methyllithium is reported to be the sole single example of this reaction type.[3] Tricyclo[5.1.0.0^{1,3}]octane (**2b**) comprises the interesting combination of a spiropentane unit and a six-membered ring.[5] In order to gain more knowledge about the reactive behavior of compounds of type **1b** (n = 3) we reexamined the reaction of **1b** and studied a similar system. We found that in both reactions *no* intramolecular addition takes place; however, products resulting from novel 1,5 C–H insertion reactions were observed instead.



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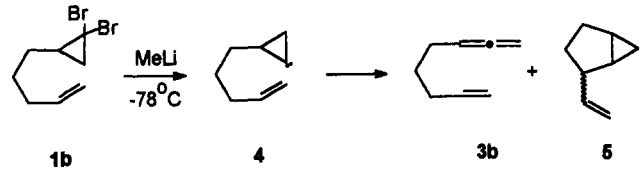
a: n = 2
b: n = 3

2 **3**

Figure 1.



1b **4** **3b** **5**

Figure 2.

Results and Discussion

1b was synthesized in 36% yield by addition of dibromocarbene ($CHBr_3$, NaOH, ultrasonication) to 1,6-heptadiene.[6] On treatment with an etheral solution of methyllithium (molar ratio 1:1.5) at −78 °C, **1b** afforded a mixture of two compounds in a ratio of 9:1.[7] The minor isomer could be separated (purity 95%) from allene **3b**[2,3] by preparative GC. NMR spectroscopic methods revealed that the minor product consisted of a mixture of two isomers of 2-ethenylbicyclo[3.1.0]hexanes **5** (ratio 6:1). On the basis of comparison with published spectral data for **5**,[8] *syn*-2-ethenylbicyclo[3.1.0]hexane is the major isomer produced. The formation of tricyclo[5.1.0.0^{1,3}]octane (**2b**), however, could not be detected.[9] The two isomeric 2-ethenylbicyclo[3.1.0]hexanes **5** result from novel 1,5 C–H insertion reactions of the cyclopropylidene in **4**. While 1,5 insertion reactions of monocyclic cyclopropylidenes into C–H bonds activated by the presence of neighboring hetero atoms (O, S, N) are documented,[1,10] insertions into allylic C–H bonds have not been observed before. In contrast, in few bicyclic systems 1,5 C–H insertions into allylic bonds have been reported.[11] Here, however, a competing intramolecular addition to the double bond would lead to extremely high-strained compounds.

The rearrangement to allene **3b** is almost the exclusive reaction pathway of **4**. In contrast, the addition of the divalent carbon and formation of tricyclic compound **2b** obviously seems to be prevented (GC detection limit: 0.05%)[9] by unfavorable steric and/or energetic conditions, thus allowing the 1,5 C–H insertion reaction to **5** to occur.

In connection with our search for new 1,n cyclodehalo-

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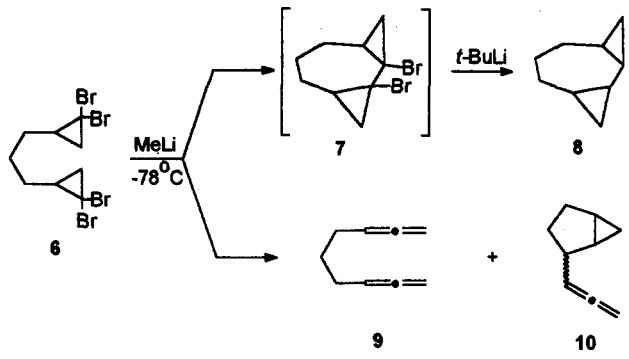

Figure 3.

genation reactions,[12] we studied the reaction of **6** with methyllithium.[3,13] **6**, in principle, can undergo a novel 1,7 cyclodehalogenation reaction to **7**. Furthermore, in light of the results obtained with **1b**, a 1,5 C–H insertion to **10** was rendered a possibility.

Addition of dibromocarbene ($CHBr_3$, *t*-BuOK) to 1,6-heptadiene gave the bisadduct **6** in 38% yield. The reaction of **6** with methyllithium (molar ratio 1:2.5) at −78 °C and subsequent GC analysis showed the formation of a product mixture which largely could be separated by preparative GC.[13] As expected, 1,2,7,8-nonatetraene (**9**)[3] was the major compound formed (isolated yield: 46%). The two isomeric 2-(1,2-propadienyl)bicyclo[3.1.0]hexanes **10** (ratio 6:1) resulting from 1,5 C–H insertions, were isolated in 12% yield. On the basis of comparison of the ^1H NMR spectra of **10** with those of **5**, as in the reaction of **1b**, the *syn*-compound is the major isomer formed. In addition, two 1-bromo-1-methyl-2-(4,5-hexadienyl)cyclopropanes and 1-bromo-2-(4,5-hexadienyl)cyclopropane could be separated in 9 and 3% yields, respectively. Furthermore, a small fraction of the reaction mixture of **6** was immediately treated with *tert*-butyllithium at −78 °C. It could be shown by GC retention time comparisons on two columns of different polarity with an independently synthesized sample that *anti*-tricyclo[6.1.0.0^{2,4}]nonane (**8**)[14] was formed in about 1%. Thus, the 1,7 cycloelimination reaction product **7** should have been present in the reaction mixture. This appears to be the first example of a 1,7-dehalogenation reaction.[12] As in the reaction of **1b**, a product resulting from an intramolecular addition to the inner double bond of the allene group formed could not be detected.

Cyclopropylidene allene rearrangements clearly dominate the reactive behavior of **6**. Besides **7** which derives from a different type of reaction, all products contain the allene subunit. The isolation of the isomeric 2-(1,2-propadienyl)bicyclo[3.1.0]hexanes **10** constitutes the second example of 1,5 C–H insertions of a monocyclic cyclopropylidene of the type described above. As in carbene **4**, the insertion of the divalent carbon takes place into the C–H bonds activated by the adjacent double bond of the allene function. In the reaction of **6**, however, it cannot be ruled out that insertion of the first-generated cyclopropylidene into the C–H bonds adjacent to the still-intact second dibromocyclopropane ring[15] and five-membered ring formation occured first, followed by a second cyclopropylidene allene rearrangement. The identical *syn*/*anti* ratios of 1,5 C–H insertion products **5** and **10** suggest, however, that similar mechanisms are operating in the reactions of **1b** and **6**. According to our calculations on the MINDO/3 level,[16] in the transition state of the 1,5 C–H insertion reaction a partial negative charge develops at the divalent carbon while a positive charge build up is generated at the allylic carbon. A similar transition state has been proposed earlier on the basis of the selectivities observed for dichlorocarbene insertions into alkanes.[17] Therefore, a double bond but possibly also heteroatoms[10,18] and three-membered rings[15] in the α-position assist in stabilizing a partial positive charge and thereby the transition state of C–H insertion reactions.

Experimental Section

General. Melting points are uncorrected. Mass spectra (electron impact) were recorded at 70 eV as *m/z*. Proton and carbon-13 NMR spectra were recorded on 400 (100.6)- and 360 (90.6)-MHz spectrometers. IR spectra were obtained on a regular and an FT instrument. All reagents were obtained commercially and used without further purification. Where dry, water-free solvents were necessary, those were distilled from lithium aluminum hydride under N_2 or Ar atmosphere. Standard laboratory glassware was used under inert atmosphere (N_2) and dried prior to use by heating and evacuating several times.

1,1-Dibromo-2-(4-pentenyl)cyclopropane (1b). Under ultrasonication 9.90 g (35.9 mmol ≡ 3.14 mol) of bromoform was added to the mixture of 3.28 g (31.4 mmol) of 1,6-heptadiene, 15 g (0.38 mol) of powdered sodium hydroxide, 50 mL of CH_2Cl_2, and a small amount of TEBA. After addition was complete (15 min), the mixture was ultrasonicated for additional 15 min. The solids were filtered over Celite and washed with CH_2Cl_2. Analytical GC showed 45% remaining 1,6-heptadiene, 50% monoadduct **1b**, and 5% bisadduct. The solvent together with the remaining educt was distilled over a 25-cm vigreux column and the residue fractionated *in vacuo*. An amount of 3.26 g (71.4%, calculated for reacted educt) of **1b** was obtained in a purity >99% (GC): ^1H NMR ($CDCl_3$, 360 MHz) 1.21 (t, 1H, *J* = 7.1 Hz), 1.43–1.70 (m, 5H), 1.70–1.79 (dd, 1H, *J* = 10.1 Hz, *J* = 7.1 Hz), 2.09–2.18 (m, 2H), 4.98 ("dd", 1H, $H_{C8,cis}$, "A" part of ABX system), 5.04 ("dd", 1H, $H_{C8,trans}$, "B" part of ABX system), 5.83 (ddt, 1H, H_{C7}, "X" part of ABX system); ^{13}C NMR ($CDCl_3$, 90.6 MHz), δ 27.6 (t), 28.6 (t), 29.4 (s, C1), 31.3 (d), 32.1 (t), 33.3 (t), 114.8 (t, C8), 138.4 (d, C7).

Reaction of 1b with Methyllithium. To the solution of 3.11 g (11.6 mmol) of **1b** in 5 mL of ether was added 20.2 mL of a 0.86 M etheral solution of methyllithium (17.4 mmol) at −78 °C. After completion (20 min) the reaction mixture was kept at −78 °C for an additional 30 min and then allowed to warm above 0 °C. Under ice cooling the mixture was hydrolyzed with 10 mL of water. The aqueous layer was separated and washed with ether. The combined organic layers were washed with water until neutral and one time with saturated brine and then dried over $MgSO_4$. Analytical GC showed 2 main products in the ratio of 6:1 (94% of the mixture). In addition, several compounds with higher retention times could be observed (6%). The ether was removed by careful distillation over a 20-cm vigreux column and the residue short-path-distilled under reduced pressure.

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Analytical samples of the two main products were obtained by preparative GC (6 ft, 20% TCEP on Chromosorb HP, 40 °C, 175 mL He/min).

1,2,7-Octatriene (3b): ^{1}H NMR (9:1 mixture with **5** in $CDCl_3$, 360 MHz) δ 1.52 ("quint", 2H), 2.02 ("nonett", 2H), 2.09 (q, 2H), 4.66 ("quint", 2H, $2H_{C1}$), 4.95 (dd, 1H, $H_{C8,cis}$), 5.01 (dd, 1H, $H_{C8,trans}$), 5.10 ("quint", 1H, H_{C3}), 5.81 (ddt, 1H, H_{C7}); ^{13}C NMR (9:1 mixture with **5** in $CDCl_3$, 90.6 MHz) 27.6, 28.3, 33.1, 74.7 (C1), 89.7 (C3), 114.6 (C8), 138.6 (C7), 208.6 (C2); GC-MS (70 eV) *m/z* 107 (5, $M^+ - 1$), 93 (94), 91 (37), 80 (34), 79 (100), 77 (43), 67 (41), 66 (30), 65 (30), 55 (12), 54 (70), 53 (38), 51 (15).

2-Ethenylbicyclo[3.1.0]hexane (5): ^{1}H NMR (6:1 mixtue of isomers in $CDCl_3$, 360 MHz) *syn*-**5** δ 0.18–0.29 (m, 2H, $2H_{C6}$), 0.87–1.00 (m, 1H), 1.18–1.28 (m, 2H), 1.47–1.66 (m, 1H), 1.67–1.79 (m, 2H), 2.68–2.79 (m, 1H, H_{C2}), 4.94 (dd, 1H, $H_{C8,cis}$, "A" part of ABX system), 5.10 (dd, 1H, $H_{C8,trans}$, "B" part of ABX system), 5.84 (ddd, 1H, H_{C7}, "X" part of ABX system); *anti*-**5** δ 0.16 ("dd", 1H, H_{C6}), 0.34 (m, 1H, H_{C6}), 1.11–1.18 (m, 1H), 1.29–1.39 (m, 1H), 2.56–2.63 (m, 1H, H_{C2}), all other signals overlap or are hidden by *syn*-**5**; ^{13}C NMR (6:1 mixture of isomers in $CDCl_3$, 90.6 MHz) *syn*-**5** δ 3.4 (t, J_{C-H} = 159 Hz, C6), 16.5 (d, J_{C-H} = 168 Hz, C1 or C5) 20.9 (d, J_{C-H} = 164 Hz, C1 or C5), 26.5 (t, J_{C-H} = 129 Hz, C3 or C4), 28.3 (t, J_{C-H} = 130 Hz, C3 or C4) 44.1 (d, J_{C-H} = 136 Hz, C2), 112.9 (t, J_{C-H} = 156 Hz, C8), 141.8 (d, J_{C-H} = 151 Hz, C7); *anti*-**5** δ 6.2 (t, J_{C-H} = 157 Hz, C6), 25.3, 26.2, 44.8 (C2), 111.9 (t, J_{C-H} = 156 Hz, C8), all other signals overlap or are hidden by *syn*-**5**; GC-MS (70 eV) *syn*-**5** *m/z* 107 (6, $M^+ - 1$), 93 (98), 91 (38), 80 (33), 79 (100), 78 (11), 77 (43), 67 (42), 66 (30), 55 (12), 54 (72), 53 (35), 51 (13); *anti*-**5** *m/z* 107 (3, $M^+ - 1$), 93 (56), 91(27), 80 (40), 79 (100), 78 (18), 77 (36), 67 (57), 66 (24), 65 (17), 54 (31), 53 (13), 51 (10).

1,3-Bis(2,2-dibromocyclopropyl)propane (6). An amount of 29.9 g (266 mmol) of potassium *tert*-butoxide was added to a solution of 3.2 g (33 mmol) of 1,6-heptadiene in ca. 150 mL of pentane. The heterogeneous mixture was stirred vigorously with a diabolo magnetic stirrer and cooled to −30 °C. An amount of 33.6 g (133 mmol) of bromoform was added (1.5 h) at that temperature. After additional stirring (30 min) the cooling bath was removed. At 0 °C the reaction mixture was poured into ice–water. The organic layer was separated and the aqueous layer washed three times with 50 mL of pentane each. The combined organic layers were washed with water until neutral and dried over $MgSO_4$. Purification was done by HPLC (RP-C_{18}, methanol/water 8:2). An amount of 5.6 g (38%) of **6** was obtained in a purity of 97.3% (GC): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 ("t", 2H), 14.5–1.85 (m, 10H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 27.1 (t), 28.4 (t), 28.5 (t), 29.2 (s), 29.2 (s), 31.2 (d), 32.1 (t), 32.2 (t) (ratio of *d,l*- and *meso*-**6** is about 1:1).

Reaction of 6 with Methyllithium. An amount of 1.7 g (3.9 mmol) of **6** was dissolved in 20 mL of ether and cooled to −78 °C. Within 30 min 6.9 mL (9.7 mmol) of a 1.4 M solution of methyllithium in ether was added. The reaction mixture was stirred at −78 °C for 1 h, then allowed to warm to 0 °C, and carefully hydrolyzed with 10 mL of water. The organic layer was separated, washed with water, and dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded 470 mg of a dark brown residue. After short-path distillation the products were separated by preparative GC (2.4 m, SE 30, 115 °C, 80 mL He/min).

1,2,7,8-Nonatetraene (9): yield 213 mg (46%), purity 98% (GC); ^{1}H NMR ($CDCl_3$, 400 MHz) 1.54 ("quint", 2H, $2H_{C5}$, *J* = 8 Hz), 1.98–2.08 ("nonett", 4H, $2H_{C4}$, $2H_{C6}$, *J* = 8 Hz), 4.63 (t, 2H, $1H_{C1}$, $1H_{C9}$, *J* = 7 Hz), 4.66 (t, 2H, $1H_{C1}$, $1H_{C9}$, *J* = 7 Hz), 5.07 ("quint", 2H, $1H_{C3}$, $1H_{C7}$, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 27.6 (t, C4, C6), 28.5 (t, C5), 74.6 (t, C1, C9), 89.6 (d, C3, C7), 208.6 (s, C2, C8); IR (film) 3060, 3030, 2980, 2930, 2860, 1950 (C=C=C), 1685, 1435, 860, 840, 755 cm^{-1}; MS (70 eV) *m/z* 120 (2, M^+), 119 (13), 105 (69), 92 (47), 91 (75), 79 (58), 78 (18), 77 (42), 67 (20), 66 (100, $M^+ - C_4H_6$), 65 (36), 54 (10), 53 (68), 52 (14), 51 (23), 50 (10), 41 (69), 39 (67).

2-(1,2-Propadienyl)bicyclo[3.1.0]hexane (10): yield 53 mg (11%), purity >99.5% after separation from **9** by preparative GC (1.8 m CW, 100 °C, 100 mL He/min), mixture of two isomers 6:1; IR (film, 6:1 mixture of isomers) 3030, 2970, 2930, 2860, 1955 (C=C=C), 1440, 1260, 865, 845 cm^{-1}. Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C 89.86; H 10.15. ^{1}H NMR (6:1 mixture of isomers in $CDCl_3$, 400 MHz): *syn*-**10** δ 0.19–0.28 (m, 2H, $2H_{C6}$), 0.90–1.03 (m, 1H), 1.17–1.38 (m, 2H), 1.53–1.67 (m, 1H), 1.67–1.80 (m, 2H), 2.68–2.79 (m, 1H, H_{C2}), 4.60–4.71 (m, 2H, $2H_{C9}$), 5.12 ("quint", 1H, H_{C7}); *anti*-**10** δ 0.15 (dd, 1H, H_{C6}, *J* = 5 Hz), 0.34 (td, 1H, H_{C6}, *J* = 5 Hz and *J* = 8 Hz), 1.45 (dd, 1H, *J* = 8 Hz, *J* = 13 Hz), 2.55–2.62 (m, 1H, H_{C2}), all other signals overlap or are hidden by *syn*-**10**; ^{13}C NMR (100.6 MHz, 6:1 mixture of isomers in $CDCl_3$) *syn*-**10** δ 3.5 (t, C6), 16.8 (d, C1 or C5), 21.6 (d, C1 or C5), 26.5 (t, C3 or C4), 27.4 (t, C3 or C4), 39.4 (d, C2), 74.8 (t, C9), 92.9 (d, C7), 207.9 (C8); *anti*-**10** δ 6.6 (t, C6), 16.3 (d, C1 or C5), 21.9 (d, C1 or C5), 25.4 (t, C3 or C4), 26.2 (t, C3 or C4), 38.6 (d, C2), 75.6 (t, C9), 95.2 (d, C7); GC-MS (70 eV, 6:1 mixture of two isomers) *syn*-**10** *m/z* 120 (2, M^+), 105 (59), 92 (58), 91 (77), 81 (45, $M^+ - C_3H_3$), 79 (100), 78 (24), 77 (70), 66 (34), 65 (19), 53 (27), 51 (19), 41 (27), 39 (50); *anti*-**10** *m/z* 120 (1, M^+), 105 (34), 92 (68), 91 (69), 81 (35), 80 (12), 79 (100), 78 (19), 77 (52), 66 (23), 65 (18), 53 (28), 51 (20), 41 (30), 40 (10), 39 (56).

1-Bromo-2-(4,5-hexadienyl)cyclopropane: yield 25 mg (3%), purity 97% (GC); IR (film) 3000, 2930, 2860, 1955 (C=C=C), 1440, 1240, 1030, 860, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.74 (dd, 1H, $1H_{C2}$), 0.97 ("sept", 1H, $1H_{C2}$), 1.13–1.40 (m, 3H, $2H_{C4}$, $1H_{C3}$), 1.52 ("quint", 2H, $2H_{C5}$), 1.97–2.08 (m, 2H, $2H_{C6}$), 2.56 ("quint", 1H, $1H_{C1}$, *J* = 4 Hz), 4.62 (t, 1H, $1H_{C9}$, *J* = 4 Hz), 4.65 (t, 1H, $1H_{C9}$, *J* = 4 Hz), 5.07 ("quint", 1H, $1H_{C7}$, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 15.9 (t, C2), 19.9 (d, C1 or C3), 22.7 (d, C3 or C1), 27.7 (t), 28.0 (t), 32.0 (t), 74.9 (t, C9), 89.7 (d, C7), 208.6 (C8); MS (70 eV) *m/z* 121, 119 (1.75, 1.9; M^+ − Br), 94 (19), 93 (29), 91 (14), 79 (100), 77 (21), 67 (69), 66 (11), 65 (13), 55 (16), 54 (15), 53 (58), 41 (45), 39 (40).

1-Bromo-1-methyl-2-(4,5-hexadienyl)cyclopropane: yield 31 mg (4%), purity 98% (GC); IR (film) 3070, 2970, 2930, 2860, 1955 (C=C=C), 1440, 1380, 1150, 1070, 1025, 1010, 865, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.38 ("t" = dd, 1H, $1H_{C2}$, *J* = 7 Hz), 1.18–1.30 (m, 2H), 1.37–1.60 (two overlapping multiplets, 4H), 1.72 (s, 3H, CH_3), 1.98–2.08 ("nonett", 2H, $2H_{C5}$, *J* = 4 Hz), 4.63 (t, 1H, $1H_{C9}$), 4.66 (t, 1H, $1H_{C9}$), 5.08 ("quint", 1H, $1H_{C7}$, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 22.9 (t, C2, *J* = 159 Hz), 24.6 (d, C3), 27.8 (t, *J* = 79 Hz), 27.9 (t, *J* = 127 Hz), 28.6 (t, *J* = 127 Hz), 33.5 (s, C1), 74.9 (t, C9), 89.7 (d, C7), 208.5 (s, C8); MS (70 eV) *m/z* 148, 146 (2.1, 2.2, $M^+ - C_5H_7$), 135 (1.6, M^+ − Br), 94 (20), 93 (26), 91 (13), 81 (19), 79 (100), 77 (18), 67 (36), 66 (11), 55 (14), 53 (47), 41 (41), 39 (30).

1-Bromo-1-methyl-2-(4,5-hexadienyl)cyclopropane: yield 42 mg (5%), purity 85% (GC); IR (film) 1955 (C=C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.57 (dd, 1H, 1 cyclopropane H), 0.70 ("t" = dd, 1H, 1 cyclopropane H, *J* = 10 Hz), 0.88 (dd, 1H, 1 cyclopropane H, *J* = 10 Hz), 1.48–1.67 (m, 4H, $2H_{C4}$, $2H_{C5}$), 1.73 (s, 3H, CH_3), 1.99–2.1 ("nonett", 2H, $2H_{C8}$, *J* = 4 Hz), 4.64 (t, 1H, H_{C9}), 4.67 (t, 1H, $1H_{C9}$), 5.10 ("quint", 1H, $1H_{C7}$, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 74.4 (t, C9), 89.9 (d, C7), 208.5 (C8), the remaining signals could not be assigned; MS (70 eV) *m/z* 148, 146 (1.85, 1.9, $M^+ - C_5H_7$), 135 (2.6, M^+ − Br), 94 (21), 93 (30), 91 (14), 81 (24), 79 (100), 77 (20), 67 (28), 66 (11), 55 (17), 53 (49), 41 (48), 39 (35).

Formation of *anti*-Tricyclo[6.1.0.0^{2,4}]nonane (8). At −78 °C ca. 1 mL of the mixture obtained from the reaction of **6** with methyllithium was diluted with 10 mL of ether, and 1 mL of a 1.5 M solution of *tert*-butyllithium in pentane was added dropwise. After 30 min at −78 °C the reaction mixture was allowed to warm to room temperature and was hydrolyzed. The organic layer was separated, washed with water until neutral, and dried over $MgSO_4$. Comparison of retention times by analytical GC on two columns of different polarity (114.5-m OV101, 120 °C and 60.5-m Marlophen 814, 80 °C) with an independently synthesized sample provides strong evidence for the formation of *anti*-**8**.

Synthesis of *syn*- and *anti*-Tricyclo[6.1.0.0^{2,4}]nonane.[13,14] The suspension of 17.36 g (0.266 mol) of zinc, 1 g (0.01 mol) of copper(I) chloride, 35.56 g (0.133 mol) of methylene iodide, and 40 mL of anhydrous ether was refluxed for 30 min. An amount of 5 g (53.1 mmol) of 1,3-cycloheptadiene was added rapidly, and the mixture was refluxed for 4 h. The heterogeneous mixture was cooled to 0 °C and ether added to a total volume of 250 mL. Pyridine was added until no more color change to yellow took place. The zinc salts were filtered off (frit D3), and the filtrate was treated again with a small amount of pyridine. After further removal of the solids, the filtrate was concentrated carefully with

a rotary evaporator. The residue was short-path-distilled (yield: ca. 11 mL), and analytical samples were separated by preparative GC (4.5-m, DC, 200°C, 140 mL He/min).

***anti*-Tricyclo[6.1.0.0^{2,4}]nonane (8):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.18–0.09 (m, 2H, $1H_{C3}$, $1H_{C9}$), 0.45–0.61 (m, 4H, $1H_{C1}$, $1H_{C2}$, $1H_{C4}$, $1H_{C8}$) 0.65–0.75 (m, 2H, $1H_{C3}$, $1H_{C9}$) 1.02–1.18 (m, 2H, $1H_{C5}$, $1H_{C7}$), 1.47–1.58 (m, 2H, $2H_{C6}$), 1.90–2.01 (m, 2H, $1H_{C5}$, $1H_{C7}$); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 12.9 (d), 13.1 (d), 13.8 (t), 25.3 (t), 27.8 (t).

***syn*-Tricyclo[6.1.0.0^{2,4}]nonane:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.02–0.12 (m, 2H), 0.37–0.48 (m, 2H) 0.88–0.99 (m, 2H) 1.00–1.18 (m, 3H), 1.35–1.48 (m, 1H), 1.69–1.80 (m, 2H), 1.80–1.93 (m, 2H).

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