Carbene−Bridgehead Olefin−Carbene Rearrangement: Formation of the Tetracyclo[4.3.0.0^{2,8}.0^{4,7}]nonane Skeleton by Carbene CH Insertion[1]

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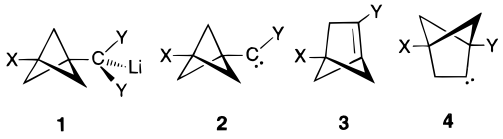
Abstract: The sequence of rearrangements of carbenes **6** has been studied. Precursors for **6** were 1-halo-3-(n-halomethyl)bicyclo[1.1.1]pentane derivatives **11**, which were obtained by addition of polyhalomethanes to the central bond of [1.1.1]propellane derivative **13** via radical chain processes. Reaction of compounds **11** with MeLi or sodium bis(trimethylsilyl)amide generates carbenes **6**, which are stabilized by a carbene (**6**)−bridgehead olefin−carbene (**9**) rearrangement, followed by an intramolecular CH insertion reaction of carbenes **9** to afford tetracyclononane derivatives **15** in good yields. The carbenes **6** show only slight preferences in the rearrangement to alkenes **7** and **8**. Both could be trapped with α-methylstyrene as ene adducts **16** and **17**. The strongly twisted bridgehead olefin **7** has only the option to rearrange to carbene **9**, whereas **8** could give **9** or **10**, but prefers to give **9**, in accordance with results of DFT calculations. The tetracyclononanes **15c** and **15d** contain halide atoms in the 1,3-positions; on treatment with *t*-BuLi both compounds form a new CC bond by reductive dehalogenation giving rise to the formation of a [2.1.1]propellane derivative **23** as short-lived intermediate.

Introduction

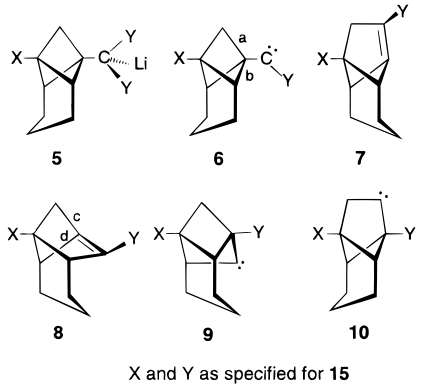
Carbenes, bound to a bridgehead position of a bicyclic or polycyclic framework, tend to rearrange to bridgehead olefins. This reaction has frequently been used by several groups to generate short-lived bridgehead alkenes. A review of this reaction has appeared recently.[2] This method has also been applied to generate highly strained alkenes, which are able to undergo a second rearrangement forming a new carbene. A prominent example of this reaction sequence is the rearrangement of cubylcarbene to homocub-1(9)-ene, which in part is further converted into homocub-9-ylidene.[3]

We have recently shown that bicyclo[1.1.1]pentyl carbenoids **1** on loss of lithium halide rearranged via carbenes **2** to bicyclo-[2.1.1]hex-1-enes **3** and that these highly strained twisted bridgehead alkenes underwent a second 1,2-bond shift to give 2-bicyclo[2.1.1]hexylidenes **4** which reacted with appropriate trapping reagents.[4] We have extended this investigation to



carbenoids of the tricyclo[4.2.0.0^{2,7}]octane system **5**. Special attention was devoted to the following questions: Which bond of carbene **6**, a or b, would migrate preferentially in the first step of the reaction sequence? Which bond of alkene **8**, bond c or d, would migrate preferentially to give carbene **9** or **10**? What are the main stabilization modes of carbenes **9** and **10**?

In addition to these problems, which could be attacked by product studies, DFT calculations on the reactive intermediates and the transition states involved in these rearrangements have been carried out to obtain some deeper insight into the chemistry of these systems. Furthermore, some of the products of the carbene−bridgehead olefin−carbene rearrangement opened the opportunity to generate [2.1.1]propellane derivatives. Reactions on this line were also carried out.



A. Synthesis of 1-Halo-8-halomethyltricyclo[4.2.0.0^{2,7}]-octanes 11. Polyhalides **11**, to be used as precursors for the generation of the carbenoids **5**, were obtained by radical chain addition of halomethanes **12** to tetracyclo[4.2.0.0^{1,7}.0^{2,7}]octane (**13**), which was prepared according to published procedures.[5] In most cases chain initiation was not necessary; the reactions

(1) Taken in part from Ströfer, T., Dissertation, Humboldt-Universität, Berlin, 1997.

(2) Jones, M., Jr. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Jai Press, Inc.: Stamford, 1998; Vol. 2, pp 77−96.

(3) Eaton, P. E.; Hoffmann, K.-L. *J. Am. Chem. Soc.* **1987**, *109*, 5285−5286. Eaton, P. E.; Appell, R. B. *J. Am. Chem. Soc.* **1990**, *112*, 4055−4057. Eaton, P. E.; White, A. J. *J. Org. Chem.* **1990**, *55*, 1321−1323. Chen, N.; Jones, M., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981−4992. See also: Hrovat, D. A.; Borden, W. T. *Mol. Phys.* **1997**, *91*, 891−895.

(4) Bunz, U.; Herpich, W.; Podlech, J.; Polborn, K.; Pratzel, A.; Stephenson, D. S.; Szeimies, G. *J. Am. Chem. Soc.* **1994**, *116*, 7637−7641.

(5) Belzner, J.; Garei*β*, B.; Polborn, K.; Schmid, W.; Semmler, K.; Szeimies, G. *Chem. Ber.* **1989**, *122*, 1509−1529.

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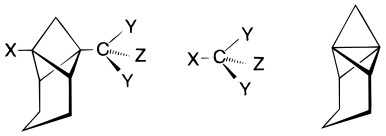
Table 1. Yields of **11**

11, **12**	X	Y	Z	% yield	**11**, **12**	X	Y	Z	% yield
a	Br	Cl	Cl	67	**d**	Br	Cl	H	61
b	Br	Br	Br	41	**e**	I	Cl	H	67
c	Br	F	Br	56	**f**	Br	Br	H	59

run to completion within 2 days at room temperature. The addition of dibromodifluoromethane (**12c**) and bromodichloromethane (**12d**) was initiated by irradiation with UV light ($\lambda \geq 300$ nm). The yields of **11** are given in Table 1. All compounds **11** could be obtained pure and were characterized by their NMR spectra.

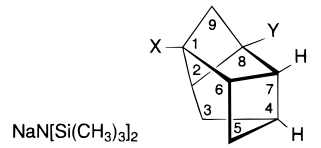


11 **12** **13**

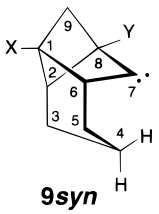
B. Generation of Type 5 Carbenoids from Halides 11 and Their Reactions. Carbenoids of type **5** were generated either by lithium halogen exchange starting from **11a** or **11b** or by metalation of **11d**, **11e**, or **11f**, using sodium bistrimethylsilylamide (**14**) as a base. The reaction mixtures were kept at room temperature for several hours. In all cases, the isolated products contained the carbon skeleton of **15**, tetracyclo[4.3.0.$0^{2,8}$.$0^{4,7}$]nonane, indicating that the expected carbene−bridgehead olefin−carbene rearrangement had taken place, followed by a C−H insertion reaction of carbene **9**. It should be noticed that CH insertion of the carbenic center in **9** into the C4−H bond can only occur from conformation **9*syn***. Yields and formation of byproducts depended strongly on the reagents used for generating carbenoid **5**. The results of various experiments of **11** with strong bases are given in Table 2.

Table 2. Reaction of **11** with Bases

11	base	solvent	products **15** (% *yield*)
a	MeLi salt-free	ether	**15a** (*46*), **15b** (*9*)
a	MeLi/LiBr	ether	**15a** (*20*), **15b** (*8*), **15c** (*21*)
b	MeLi salt-free	ether	**15c** (*54*), (trace of **15b**)
d	**14**	THF/ether	**15a** (*64*)
e	**14**	THF/ether	**15d** (*73*)
f	**14**	THF/ether	**15c** (*88*)



15	X	Y
a	Br	Cl
b	Br	Me
c	Br	Br
d	I	Cl
e	H	H
f	H	Br
g	Br	H
h	H	Cl



9*syn*

As seen from Table 2, all isolated compounds are derived from **15**, indicating that carbene **9** was heavily involved in product formation. No evidence for the intermediacy of carbene **10** was obtained from our product studies. This could mean that only bridgehead olefin **7** is involved in the reaction sequence or, if olefin **8** is also formed, **8** shows a significant preference for bond c over bond d migration to the Y-carrying C atom. With this premise, it is conceivable that **7** might not be involved at all.

Carbenoid formation by metalation starting from **11d**, **11e**, or **11f** and using the base **14** gives higher yields of **15** free of side products. To the best of our knowledge, the carbon framework of **15** has not been synthesized so far. The reaction shown here is an efficient access to this tetracyclic system. The hydrocarbon tetracyclo[4.3.0.$0^{2,8}$.$0^{4,7}$]nonane (**15e**) was obtained from dibromide **15c** in 73% yield by reduction with tri-*n*-butyltin hydride under irradiation for 8 h. Shorter reaction times led to **15e** and a mixture of the monobromides **15f** and **15g**, which could not be separated.

The structure of the new carbon skeleton rests on the NMR spectra. The most significant evidence for structure **15** was obtained from an INADEQUATE experiment of **15a** and **15c**. The $^{13}C^{13}C$ coupling constants of **15a** and **15c** are given in Table 3.

Table 3. $^{13}C^{13}C$ Coupling Constants of **15A** and **15c** (in Hz)

	$J(^{13}C^{13}C)$			$J(^{13}C^{13}C)$	
bonding pair	**15a**	**15c**	bonding pair	**15a**	**15c**
C1−C2	26.5	26.5	C4−C5	28.3	28.3
C1−C6	30.1	31.8	C4−C7	28.3	28.3
C1−C9	28.3	28.3	C5−C6	30.1	28.3
C2−C3	33.6	33.6	C6−C7	23.0	21.2
C2−C8	24.8	24.8	C7−C8	37.2	*a*
C3−C4	31.8	31.8	C8−C9	31.8	30.1

[a] This coupling constant could not be determined with certainty.

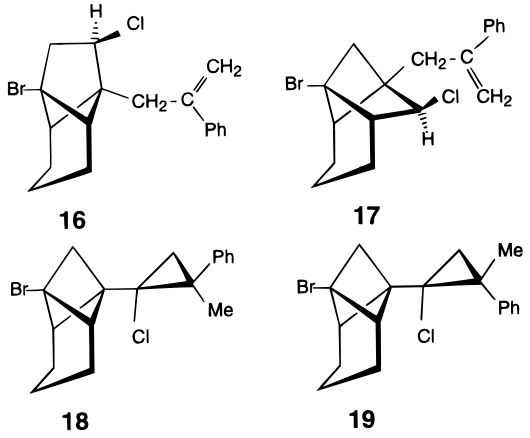
The formation of **15b** in the reaction of **11a** with MeLi, salt-free or mixed with LiBr (first and second entry of Table 2), needs some comment. In a control experiment, in which **15c** was reacted with an excess of MeLi/LiBr, and which led to the re-isolation of **15c** in 90% yield, it was shown that the introduction of the methyl group did not take place via **15c**, but on an earlier stage of the reaction sequence. Presumably it is carbenoid **5**, which will react with MeLi, either directly by exchange of bromide against methyl, or via carbene **6** by addition of MeLi. In either case, the intermediate carbenoid could lose lithium halide and produce the modified carbene **6** (X = Br, Y = Me), which could undergo the sequence of rearrangements discussed above and afford **15b**. We have recently shown that this is the major route for Me incorporation when **1** or **2** is generated in the presence of MeLi.[6] The formation of **15c** in the reaction of **11a** with MeLi/LiBr (second entry of Table 2) can be interpreted on the same line.

C. Trapping Experiments of Intermediates in the Rearrangement Sequence. So far, carbene **9** is the only intermediate whose existence has been established by the intramolecular CH insertion to afford **15**. In earlier related investigations, we were able to show that type **9** carbenes could be trapped by suitable reagents.[4] For this reason, **11b** and MeLi/LiBr were allowed to react in the presence of cyclohexene or tetramethylethylene. NMR analysis of the products gave no indication for the formation of cycloadducts of carbenes **9** or **10** to cyclohexene or tetramethylethylene.

Recently, generation of bicyclo[2.1.1]hex-1-enes in the presence of α-methylstyrene afforded a 1:1 adduct produced by an ene reaction.[6] The same trapping reagent was added to the reaction of **11b** with MeLi (salt-free) and on standard workup, a 6% yield of an approximate 1:1 mixture of the formal ene

(6) Ströter, Th.; Jarosch, O.; Szeimies, G. *Eur. J. Chem.* **1999**, *5*, 2046−2055.

adducts **16** and **17** was isolated. HPLC separation afforded these compounds sufficiently pure to obtain NMR spectra from which the structures could be determined by one- and two-dimensional

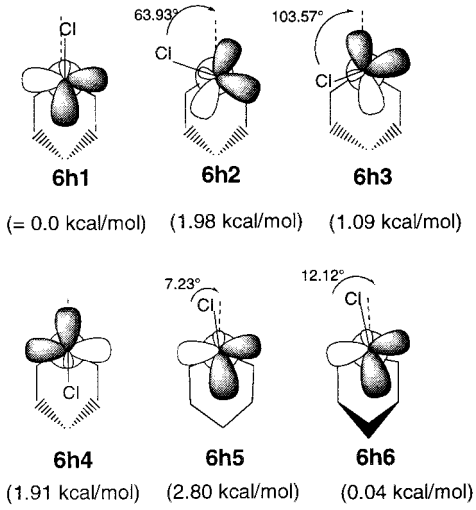


COSY and HETCOR pulse sequences. In addition to **16** and **17**, the stereoisomers **18** and **19** were also observed in low yield, whose formation is attributed to the addition of carbenoid **5** or carbene **6** (X = Br, Y = Cl) to α-methylstyrene.

The formation of **16** and **17** indicates that both bridgehead olefins **7** and **8** are involved in the reaction paths.

D. DFT Calculations on the Carbene 6h−Bridgehead Olefin 7h/8h−Carbene 9h/10h Rearrangement. We have shown experimentally that carbene **6** rearranges via two routes to the bridgehead olefins **7** and **8**. Whereas olefin **7** can only lead to carbene **9**, **8** obviously prefers one of the two possible rearrangements and selectively forms carbene **9**. An alternative possibility could be that all of carbene **9** comes from alkene **7** and that alkene **8** would not rearrange further. The following calculations were carried out on the reactive intermediates **6h**, **7h**/**8h**,and **9h**/**10h**, on the transition states separating these molecules, and on the final products to learn more about the energetics of the interchanging molecules and on the barriers of interconversion. The Gaussian 94 program package[7] has been used preferentially. Density functional theory (DFT)[8,9,10] with Becke's three-parameter hybrid method and the exchange functional of Lee, Yang, and Parr was employed. Geometry optimizations were carried out with the 6-31G(d) basis set and frequency calculations were performed at the same level of theory, allowing the characterization of the stationary points as minima or transition structures. The energies of the stationary points were recalculated with the 6-311G(d, p) basis set on the 6-31G(d) structures. These energies were corrected for the 6-31G(d) zero-point energies, which were scaled by a factor of 0.9804, as recommended in the literature.[11] For carbenes **6h** and **9h**/**10h** and for products **15h**, **20**, and **21**, the restricted formalism was employed. For transition states and for bridgehead olefins **7h**/**8h** the unrestricted procedure was used. All transition states gave $\langle S^2 \rangle$ values of zero and identical results as the restricted formalism. Due to the biradical nature of the bridgehead olefins, $\langle S^2 \rangle_b$ values (before spin annihilation) of close to 1.0 were computed. After spin annihilation, $\langle S^2 \rangle_a$ values dropped to 0.03−0.06, indicating that the projected wave function might be regarded as reasonable for the singlet state of the twisted alkenes **7h** and **8h**.[12] The results, including $\langle S^2 \rangle_b$ and the $\langle S^2 \rangle_a$ values for the bridgehead alkenes, are given in Table 4.

According to the results of Table 4, for carbene **6** local energy minimum conformations **6h1**, **6h3** (and its mirror image), and **6h6** (and its mirror image) could be found. The rotational barrier at the carbene carbon atom between conformation **6h1** and **6h3** is 2.0 kcal/mol, and 0.9 kcal/mol in the reverse direction. The trimethylene bridge is flexible and can take a transoid conformation as in **6h1** or a cisoid arrangement as in **6h6**. At 0.04 kcal/mol, the energy difference is negligible. The barrier {E(**6h5**) − E(**6h1**)} separating these conformations amounts to 2.8 only kcal/mol.



The structure of **6h1**, computed without any symmetry restriction, was close to C_s symmetry. This geometry leads to an efficient interaction of a π-like orbital of the bicyclo[1.1.1]-pentane framework, located at C1C2 and C1C6, with the empty p-orbital of the carbenic center. C2 or C6 will be the migrating atom to reach transition state **TSI2**, and finally bridgehead olefin **8h1** (see Figure 1, first column). In conformation **6h3**, the dihedral angle Cl−C9−C1−C8 is −103.6°, which leads to a favorable interaction of the carbene p-orbital with the bond C1C8. C8 will be the migrating atom within the rearrangement process, which passes over **TSI1** to give bridgehead alkene **7h1** (second column of Figure 1). The energy barrier from **6h3** to olefin **7h1** has been calculated as 7.7 kcal/mol, the barrier of **6h1** to olefin **8h1** as 6.6 kcal/mol.

Both olefins are strongly pyramidalyzed. For **7h1**, the dihedral angle Cl−C9−C8−C7 was computed as 132.4°, for **8h1**, the dihedral angle Cl−C7−C6−C1 was −130.3°. In addition to the structures of **7h1** and **8h1**, these olefins can populate the conformations **7h2** and **8h2**, **8h3**, and **8h4**, the structures and energies of which have also been calculated. The relative energies are shown below the formulas.

(7) *Gaussian 94* (Revision D.3); Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(8) Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974−12980.

(9) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(10) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *37*, 785.

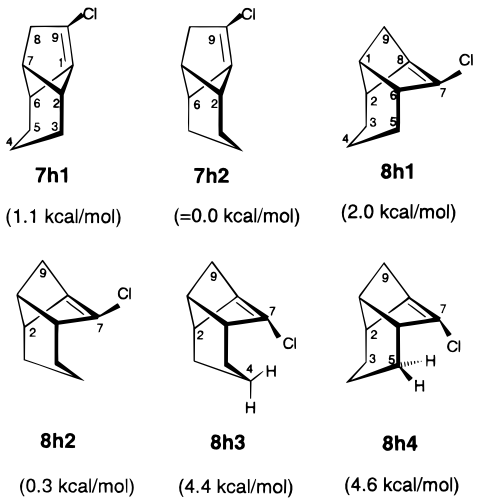
(11) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian Inc.: Pittsburgh, 1996; p 64 and references therein.

(12) For a discussion of unrestricted DFT methods on molecules with biradical character in their singlet states, see: Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036−6043 and references therein. See also: Hrovavat, D. A.; Duncan, J. A.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 169−175.

Table 4. Energies (B3LYP/6-31G(d)//B3LYP/6-31G(d) and B3LYP/6-311G(d,p)//B3LYP/6-31G(d)) and Zero-Point Energies for Carbenes **6h**, Alkenes **7h** and **8h**, Carbenes **9h** and **10h**, Hydrocarbons **15**, **20**, and **21**, Transtion States **TSI**, **TSII**, and **TSIII**, and **7h** and **8h**; $\langle S^2\rangle_a/\langle S^2\rangle_b$ Values for Alkenes **7** and **8**

molecule	*E*[B3LYP/6-31G(d)// B3LYP/6-31G(d)], au; $\langle S^2\rangle_a/\langle S^2\rangle_b$	zero-point energy (no. of imaginary freq), au[a]	*E*[B3LYP/6-311G(d,p)// B3LYP/6-3G(d)], au[b]
6h1	−809.587683	0.172986 (0)	−809.527265
6h2	−809.584021	0.172498 (1)	−809.524113
6h3	−809.585990	0.172967 (0)	−809.525523
6h4	−809.583306	0.172447 (1)	−809.524219
6h5	−809.582934	0.172689 (1)	−809.522809
6h6	−809.587905	0.172891 (0)	−809.527205
TSI1 (6h3 → 7h1)	−809.572369	0.172258 (1)	−809.513225
TSI2 (6h1 → 8h1)	−809.575996	0.172533 (1)	−809.516771
7h1	−809.610550; *0.8518/0.0365*	0.173735 (0)	−809.548776
7h2	−809.612308; *0.8407/0.0356*	0.173638 (0)	−809.550594
8h1	−809.609543; *0.8282/0.0338*	0.174079 (0)	−809.547343
8h2	−809.612132; *0.8222/0.0332*	0.173979 (0)	−809.550101
8h3	−809.606033; *0.9797/0.0607*	0.173946 (0)	−809.543577
8h4	−809.605722; *0.9497/0.0528*	0.174186 (0)	−809.543278
TSII1 (7h1 → 9h1)	−809.595370	0.172529 (1)	−809.538092
TSII2 (7h2 → 9h2)	−809.597880	0.172423 (1)	−809.540604
TSII3 (8h1 → 9h1)	−809.590185	0.172813 (1)	−809.532535
TSII4 (8h2 → 9h2)	−809.595451	0.172797 (1)	−809.537709
TSII5 (8h3 → 10h)	−809.584620	0.172302 (1)	−809.528045
TSII6 (8h4 → 10h)	−809.587740	0.172817 (1)	−809.529920
9h1	−809.613337	0.173510 (0)	−809.554057
9h2	−809.619830	0.173608 (0)	−809.559870
10h	−809.617769	0.173058 (0)	−809.559121
TSIII1	−809.604302	0.170409 (1)	−809.549277
TSIII2	−809.598574	0.171207 (1)	−809.542282
TSIII3	−809.590742	0.170557 (1)	−809.535396
15h	−809.716315	0.176634 (0)	−809.650798
20	−809.706792	0.176409 (0)	−809.642015
21	−809.708275	0.176129 (0)	−809.643444

[a] ZPE scaled by a factor of 0.9804. [b] Corrected for ZPE.

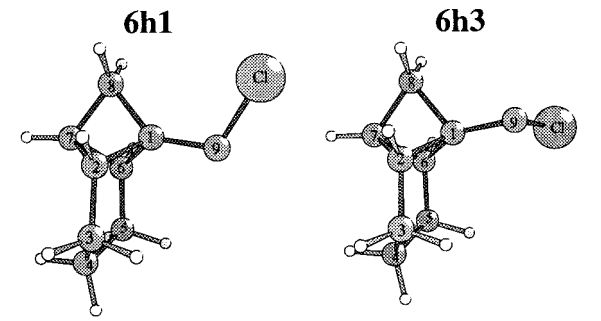


The conformational preferences of bridgehead alkenes **7** and **8** are based on the preferred chair conformation of the cyclohexane ring in these molecules. The "unimpaired" chair in **7h2** makes this conformation energetically slightly better than **7h1**. The differences in energy are somewhat greater between chair **8h2** and boat **8h1** and **8h4**. In the chair conformation **8h3** there is an unfavorable repulsive interaction between the chlorine atom and the axial hydrogen at C4 (distance 2.69 Å).[13] Another repulsive interaction between the chlorine atom and the axial hydrogen of C5 (distance 2.74 Å) and of C3 (distance 2.88 Å) seems to be responsible for the rise in energy of **8h4**.

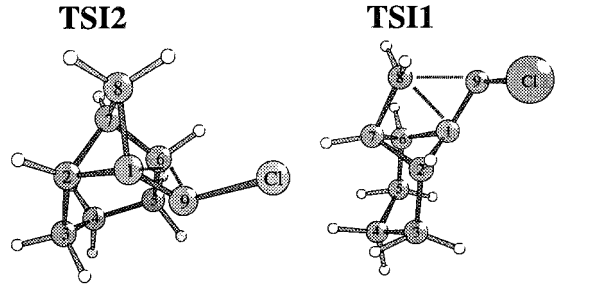
(13) The sum of the van der Waals radii of chlorine and hydrogen is 2.95 Å. See: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

A further point of interest is the barrier of inversion of **8h1** → **8h4**. As the transition state for this inversion is a biradical, we have chosen the CAS(2,2)MP2/6-31G(d) formalism as implemented in Gaussian 94. The energy barrier **8h1** → **8h4** was calculated as 6.42 kcal/mol (**8h1**: $E = -807.868492$; ZPE = 0.191261(0); **TS**: $E = -807.857069$; ZPE = 0.190076(1); **8h4**: $E = -807.861965$; ZPE = 0.191268(0)). This value suggests that the π bonding energy in the bridgehead olefin **8h** is reduced to approximately 10% of its value in undistorted olefins.

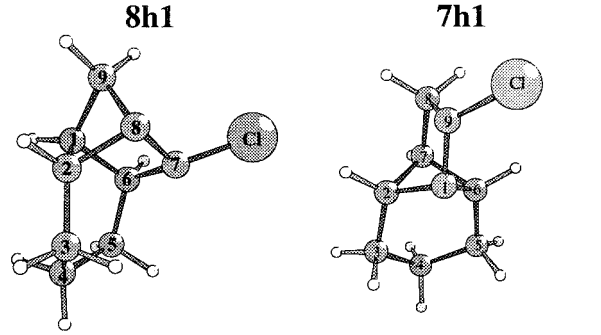
The energetically preferred 1,2-alkyl shift in the olefins **7** and **8** takes place under inversion of configuration at the pyramidalyzed C9 and, respectively, C7.[6] For **7h1** and **7h2**, C2 is the migrating carbon atom, for **8h1** and **8h2** C9 will be shifted to C7, whereas for **8h3** and **8h4** a new bond will be formed between C2 and C7. Bridgehead olefin **7** can only rearrange to carbene **9h**; olefin **8h**, however, can give carbene **9h** or carbene **10h**. We have been able to locate the six transition structures which are depicted in Figure 2. The relative energies are shown under the computer-generated structures. The structures and the relative energies reveal that the steric effects influencing the energies of the bridgehead olefins **7h** and **8h** are also present in the transition structures **TSII1** to **TSII6**, shifting **TSII3**, **TSII5,** and **TSII6** to higher energies than their counterparts. Transition structures **TSII5** and **TSII6** are the only stationary points leading to carbene **10h**; their increased energy prevents this carbene from being formed, in accordance with our experimental observations. The lowest barrier for the reaction of alkene **7h** (**TSII2-7h2**) has been calculated to be 6.3 kcal/mol, and for the reaction of **8h** (**TSII2-8h2**) 7.8 kcal/mol, whereas the **TSII6-8h2** barrier is as high as 12.7 kcal/mol. This



Selected Structural Data:		Selected Structural Data:	
1-9	1.4507 Å	1-9	1.4554 Å
1-2	1.5992 Å	1-2	1.5759 Å
1-6	1.5991 Å	1-6	1.5732 Å
1-8	1.5571 Å	1-8	1.5920 Å
Cl-9-1	110.19°	Cl-9-1	109.52°
Cl-9-1-8	0.01°	Cl-9-1-8	-103.57°



Selected Structural Data:		Selected Structural Data:	
1-6	1.9073 Å	1-8	1.8493 Å
6-9	1.9753 Å	8-9	1.8880 Å

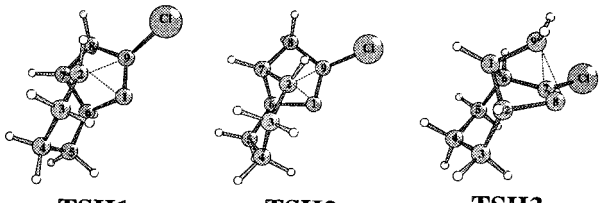


Selected Structural Data:		Selected Structural Data:	
7-9	1.4492 Å	1-9	1.4497 Å
2-8	1.5470 Å	1-2	1.5459 Å
8-9	1.5566Å	1-6	1.5683 Å
Cl-7-6-1	-130.32°	Cl-9-8-7	132.41°

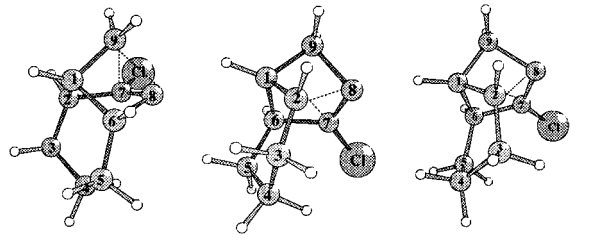
Figure 1. B3LYP-6-31G(d) structures of **6h1**, **TSI2**, and **8h1** and **6h3**, **TSI1**, and **7h1**.

energy difference explains well the experimentally observed selectivity in the rearrangement of carbene **8**.

Carbene **9h2** with the cyclohexane subunit in the chair conformation was found to be more stable by 3.6 kcal/mol than **9h1**. This supports the CH insertion of the carbenic center C7 into the axial 4-H. The barrier of this reaction was determined to be 6.8 kcal/mol. Intramolecular competition could be envisioned by insertion of C7 into CH bonds of C5 or C3. This could reasonably occur only from the energetically unfavorable **9h1** conformer by insertion into the respective axial CH bonds

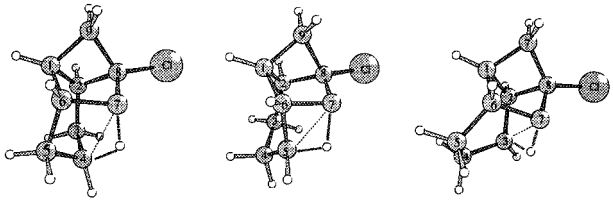


TSII1	TSII2	TSII3
E_{rel} =1.6 kcal/mol	E_{rel} ≡0.0 kcal/mol	E_{rel} =5.1kcal/mol
1-2 1.8296 Å	1-2 2.1260 Å	7-9 2.0482 Å
2-9 2.1183 Å	2-9 1.8680 Å	8-9 1.8019 Å



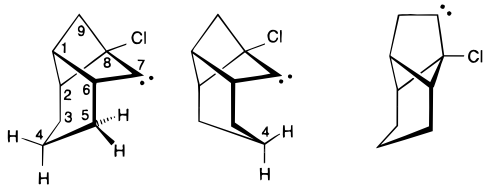
TSII4	TSII5	TSII6
E_{rel} =1.8 kcal/mol	E_{rel} =7.9kcal/mol	E_{rel} = 6.7kcal/mol
7-9 2.0558 Å	2-7 2.2610 Å	2-7 2.1944 Å
8-9 1.7934 Å	2-8 1.8151 Å	2-8 1.7839 Å

Figure 2. B3LYP/6-31G(d) transition structures **TSII1** to **TSII6**.



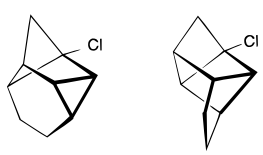
TSIII1	TSIII2	TSIII3
E_{rel} ≡0.0 kcal/mol	E_{rel} = 4.4 kcal/mol	E_{rel} = 8.7 kcal/mol
4-7 2.2102 Å	5-7 1.9424 Å	3-7 2.1675 Å
H-4 1.3267 Å	H-5 1.2380 Å	H-3 1.2768 Å
H-7 1.3016 Å	H-7 1.4284 Å	H-7 1.3369 Å

Figure 3. B3LYP/6-31G(d) transition structures **TSIII1**−**3**.



9h1 **9h2** **10h**

at C5 and C3 leading to **20** and **21**. All three transition structures have been located and are depicted in Figure 3. From their relative energies (see Figure 3) it can be deduced that the formation of **15** is strongly favored over the CH insertion affording **20** and **21**. In addition we computed **15h** to be more stable by 5.5 kcal/mol than **20** and by 4.6 kcal/mol than **21**.

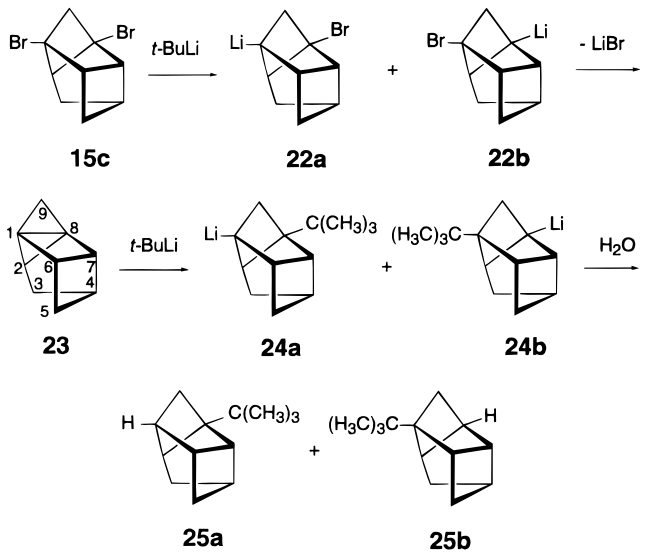


20 **21**

Summing up the results of section D, it has been shown that the rearrangement of carbene **6h** will generate bridgehead olefins **7h** and **8h**. Whereas **7h** can only afford carbene **9h**, the

rearrangement of **8h** to carbene **9h** is energetically considerably favored over the formation of carbene **10h**. **9h** will preferentially insert into the CH bond of C4 leading to the tetracyclic compound **15h**. These results are in accordance with experiment.

Scheme 1



F. Generation of Pentacyclo[4.3.0.0^{1,6}.0^{2,8}.0^{4,7}]nonane (23). The effective access of the dihalides **15c** and **15d** prompted us to investigate their reaction with an excess of *t*-BuLi. It could be expected that this reaction would lead to the [2.1.1]propellane derivative **23**. Although the parent [2.1.1]propellane has been observed spectroscopically by low-temperature matrix isolation technique,[14] neither the parent nor derivatives of it have been isolated, although their intermediacy has been invoked in several cases.[15,16] Under the premise that **23** cannot be isolated, a trapping reagent had to be present in the formation reaction of **23**. *t*-BuLi was used successfully as a trapping reagent in this case. The mixture of **15c** and 3 equiv of *t*-BuLi afforded after aqueous workup a 1.7:1.0 mixture of **25a** and **25b** in 49% yield. The mixture could be analyzed by analytical GC; preparative GC gave only a partial separation, leading to the isolation of two different fractions (**25a**:**25b** 6:1 and 0.67:1), whose NMR spectra allowed the structural assignments. The proposed reaction mechanism is shown in Scheme 1. This mechanism was supported by the reaction of dihalide **15d** with 3 equiv of *t*-BuLi. After aqueous workup, the ratio of products **25a**:**25b** was again determined to be 1.7:1.0. This result is consistent with the interpretation that a common intermediate is involved in both reactions, which could only be [2.1.1]propellane **23**.

Conclusions

Carbenes of type **6**, generated by loss of lithium halide of carbenoids **5**, rearrange by migration of CH_2 or CH to the carbenic carbon with formation of bridgehead olefins **7** and **8**. Our results indicate that the selectivity for these rearrangements is low. In a consecutive rearrangement bridgehead olefin **7** forms carbene **9**, which is also generated selectively from alkene **8**. Carbene **9** is stabilized by CH insertion into the axial 4-H bond affording tetracyclic compound **15**. Results of DFT calculations on the rearrangement of **8** → **9** and on the alternative CH insertion reactions of carbene **9** are in accordance with the experimental results. Dihalides **15** are valuable precursors for [2.1.1]propellane derivative **23** as a fleeting intermediate.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra including ^{1}H^{1}H COSY, ^{1}H^{13}C HETCOR, and ^{13}C^{13}C INADEQUATE measurements were recorded on Bruker AM 300, Bruker DPX 300, Bruker AMX 600, and Varian 400S with TMS as an internal standard. Infrared spectra were obtained on a Perkin-Elmer 881, and mass spectra on a Finnigan MAT 90. Melting points were determined on a Büchi 530 and are uncorrected. Microanalyses were carried out at the Humboldt Universität, Institut für Chemie, Microanalytical Laboratory. Reactions were monitored by thin-layer chromatography (TLC) using analytical silica gel 60 F_{254} on aluminum foil by Merck (Darmstadt) and visualized with ammonium molybdate solution or by UV light. Preparative column chromatography was carried out on glass columns of different size, packed with Merck (Darmstadt) silica gel 60 (230−400 mesh ASTM) or Merck silica gel 40 (35−70 mesh ASTM).

Analytical gas chromatography was performed using a Varian Star 3400 CX and a Shimadzu GC 14A; preparative gas chromatography was carried out on a Siemens RGC 202 equipped with silicon OV-1 columns (10% on chromosorb; 4 m, 5.33 mm diameter).

Materials. *n*-Butyllithium (BuLi) was purchased from Chemetall, Frankfurt/M, Germany, as a 1.6 M solution in hexane and *tert*-butyllithium (*t*-BuLi) from Acros and Aldrich as a 1.6 or 1.7 M solution in pentane. Methyllithium (MeLi) containing LiBr in ether was prepared from bromomethane and Li according to standard procedures. MeLi, salt-free (1.6 M in ether), and sodium bis(trimethylsilyl)amide (**14**, 1.0 M in THF) were obtained from Aldrich.

Tetracyclo[4.2.0.0^{1,7}.0^{2,7}]octane (**13**) was prepared as reported earlier.[5]

Synthesis of 1-Halo-7-(n-halomethyl)tricyclo[4.2.0.0^{2,7}]octanes 11. (a) 1-Bromo-7-trichloromethyltricyclo[4.2.0.0^{2,7}]octane (**11a**). Tetracyclus **13** (2.20 g, 20.7 mmol) was mixed under nitrogen with bromotrichloromethane (**12a**) (12.6 g, 63.5 mmol) and the solution was stirred at room temperature for 48 h. The excess of **12a** was removed in vacuo and the oily residue purified by column chromatography in petroleum ether, affording **11a** (5.02 g, 80%) as colorless oil, which was distilled at 50 °C/2.0 × 10^{-5} mbar to give 4.21 g (67%) of **11a** as a waxy solid of mp 30 °C.

IR (KBr): $\tilde{\nu}$ 2946, 2925, 2910, 2877, 2863, 1470, 1444, 1241, 1178, 1154, 1129, 1108, 963, 883, 854, 790, 785, 742, 735, 678 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50−2.40 (m, 6 H, 3-, 4-, 5-H_2), 2.26 (s, 2 H, 8-H_2), 2.95 (m, 2 H, 2-, 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.87 (t, C-4), 18.55 (t, C-3, C-5), 40.97 (s, C-1), 53.57 (s, C-7), 55.60 (t, C-8), 63.00 (d, C-2, C-6), 96.33 (s, *C*Cl_3). MS (70 eV, EI): *m*/*z* (%) 269 (1), 267 (1, M^+ − Cl), 189 (22), 188 (8, M^+ − Br − Cl), 187 (38), 153 (32), 152 (27), 151 (67), 117 (45), 116 (50), 105 (44), 91 (39), 79 (41), 77 (59). $C_9H_{10}BrCl_3$ (304.44): calcd C 35.51, H 3.31; found C 35.57, H 3.41.

(b) 1-Bromo-7-tribromomethyltricyclo[4.2.0.0^{2,7}]heptane (**11b**). **13** (1.89 g, 17.8 mmol) and tetrabromomethane **12b** (7.00 g, 21.1 mmol) were dissolved at −78 °C in ether (10 mL) and kept at room temperature under nitrogen for 48 h. Column chromatographic workup (petroleum ether) afforded **11b** (3.19 g, 41%) as a solid of mp 81−82 °C.

IR (KBr): $\tilde{\nu}$ 2949, 2938, 2924, 2901, 2858, 1441, 1224, 1178, 1150, 1095, 954, 880, 752, 734, 688, 682, 674, 654 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62−1.91, 2.23−2.38 (m, 6 H, 3-, 4-, 5-H_2), 2.33 (s, 2 H, 8-H_2), 2.97 (m, 2 H, 2-, 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.62 (t, C-4), 18.40 (t, C-3, C-5), 36.49, 39.80 (2 s, C-1, C-7), 55.83 (s, *C*Br_3), 57.66 (t, C-8), 63.43 (d, C-2, C-6). MS (70 eV, EI): *m*/*z* (%) 280 (2), 279 (3), 278 (3), 277 (6), 276 (2, M^+ − 2 Br), 118 (37), 117 (100), 116 (53), 115 (48), 91 (51), 81 (48), 79 (67), 77 (32). $C_9H_{10}Br_4$ (437.79): calcd C 24.69, H 2.30, Br 73.01; found C 24.45, H 2.73, Br 73.74.

(c) 1-Bromo-7-bromodifluoromethyltricyclo[4.2.0.0^{2,7}]octane (**11c**). **13** (2.19 g, 20.6 mmol) and dibromodifluoromethane **12c** (12.6 g, 60.1 mmol) were mixed in a quartz Schlenk tube at −78 °C and irradiated at room temperature for 1 h with an UV quartz lamp using a filter ($\lambda \geq$ 300 nm). The solution was kept at room temperature for 48 h.

(14) Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638−3641.
(15) Morf, J.; Szeimies, G. *Tetrahedron Lett.* **1986**, 5363−5366.
(16) Fuchs, J.; Szeimies, G. *Chem. Ber.* **1992**, *125*, 2517−2522.

Distillative workup afforded **11c** (3.62 g, 56%) as a colorless liquid of bp 25 °C/2 × 10^{-5} mbar.

IR (film): $\tilde{\nu}$ 2949, 2910, 1390, 1308, 1267, 1184, 1158, 1133, 1112, 1088, 1057, 1042, 1028, 955, 895, 883, 863, 796, 601 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.48−1.91 (m, 6 H, 3-, 4-, 5-H_2), 2.20 (s, 2 H, 8-H_2), 2.87 (m, 2 H, 2-, 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.05 (t, C-4), 18.98 (t, C-3, C-5), 41.47 (s, C-1), 48.08 (t, $^2J_{CF}$ = 28.2 Hz, C-7), 54.27 (t, C-8), 63.06 (d, C-2, C-6), 118.81 (t, $^1J_{CF}$ = 304.0 Hz, *C*BrF_2). MS (70 eV, EI): *m*/*z* (%) 237 (2), 235 (2, M^+ − Br), 156 (29), 155 (100), 136 (24), 135 (65), 127 (81), 115 (51), 109 (32), 105 (30), 91 (98), 79 (35), 77 (68). $C_9H_{10}Br_2F_2$ (315.98): calcd C 34.21, H 3.19, Br 50.58; found C 34.45, H 2.73, Br 50.24.

(d) 1-Bromo-7-dichloromethyltricyclo[4.2.0.0^{2,7}]octane (11d). 13 (2.20 g, 20.7 mmol) and bromodichloromethane **12d** (10.4 g, 63.5 mmol) were allowed to react as described for **11c**. Distillative workup afforded **11d** (3.40 g, 61%) as a colorless oil of bp 20 °C/10^{-3} mbar.

IR (film): $\tilde{\nu}$ 2943, 2926, 2908, 2903, 2855, 1476, 1463, 1444, 1387, 1262, 1215, 1177, 1154, 1121, 967, 946, 886, 784, 765, 738, 649, 601 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.73 (m, 6 H, 3-, 4-, 5-H_2), 2.19 (s, 2 H, 8-H_2), 2.74 (m, 2 H, 2-, 6-H), 5.92 (s, 1 H, C*H*Cl_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.20 (t, C-4), 19.12 (t, C-3, C-5), 43.19,-47.81 (2 s, C-1, C-7), 52.53 (t, C-8), 62.11 (d, C-2, C-6), 69.21 (d, *C*HCl_2). MS (70 eV, EI): *m*/*z* (%) 237 (1), 235 (2), 233 (1, M^+ − Cl), 199 (2), 197 (2), 193 (2), 191 (3), 189 (3, M^+ − Br), 153 (31), 125 (43), 117 (98), 115 (41), 105 (32), 91 (100), 79 (52), 77 (72). C_9H_{11}-$BrCl_2$ (270.00): calcd C 40.04, H 4.11; found C 41.08, H 3.92.

(e) 1-Iodo-7-dichloromethyltricyclo[4.2.0.0^{2,7}]octane (11e). 13 (1.70 g, 16.0 mmol) and iododichloromethane **12e** (5.00 g, 23.7 mmol) were mixed at −78 °C and kept under N_2 for 48 h at room temperature. The excess of **12e** was removed at 0 °C/2.0 ×10^{-5} mbar and the dark-green residue purified by column chromatography with petroleum ether, leading to **11e** (3.38 g, 67%) as a yellow oil.

IR (film): $\tilde{\nu}$ 2943, 2904, 2870, 2852, 1443, 1258, 1246, 1214, 1174, 953, 884, 764, 735, 600 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.54−1.81 (m, 6 H, 3-, 4-, 5-H_2), 2.25 (s, 2 H, 8-H_2), 2.76 (m, 2 H, 2-, 6-H), 5.89 (s, 1 H, C*H*Cl_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.91 (t, C-4), 18.72 (s, C-1), 20.03 (t, C-3, C-5), 51.27 (s, C-7), 52.99 (t, C-8), 63.17 (d, C-2, C-6), 68.85 (d, *C*HCl_2). MS (70 eV, EI): *m*/*z* (%) 191 (2), 189 (4, M^+ − I), 127 (28), 117 (100), 115 (30), 91 (70), 77 (40). C_9H_{11}-Cl_2I (317.00): calcd C 34.10, H 3.50, Cl 22.37; found C 34.03, H 3.45, Cl 22.65.

(f) 1-Bromo-7-dibromomethyltricyclo[4.2.0.0^{2,7}]octane (11f). 13 (4.41 g, 41.5 mmol) and bromoform **12f** (70.5 g, 280 mmol) were reacted as described for **11e**, affording **11f** (8.72 g, 59%) as a pale yellow oil. Neither further column chromatography nor preparative GC (decomposition!) led to pure material.

IR (film): $\tilde{\nu}$ 3000, 2942, 2871, 2854, 2837, 1464, 1443, 1255, 1224, 1177, 1156, 1144, 1118, 1094, 964, 673, 658, 601 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.71 (m, 6 H, 3-, 4-, 5-H_2), 2.20 (s, 2 H, 8-H_2), 2.70 (m, 2 H, 2-, 6-H), 5.89 (s, 1 H, C*H*Br_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.22 (t, C-4), 19.03 (t, C-3, C-5), 41.02 (d, *C*HBr_2), 42.34, 49.12 (2 s, C-1, C-7), 53.74 (t, C-8), 62.23 (d, C-2, C-6). MS (70 eV, EI): *m*/*z* (%) 281 (2), 279 (3), 277 (2, M^+ − Br), 117 (48), 115 (36), 105 (31), 95 (43), 91 (95), 82 (86), 81 (69), 80 (86), 79 (100), 77 (61). $C_9H_{11}Br_3$ (358.90): calcd C 30.12, H 3.09; found C 31.88, H 3.47.

Reaction of 11 with Strong Bases. (a) 11a and MeLi, salt-free: To a solution of **11a** (3.04 g, 9.99 mmol) in ether (15 mL) kept in a dry ice bath at −78 °C was added dropwise a solution of MeLi salt-free (32.0 mL, 1.6 M, 51.2 mmol) in ether with stirring under nitrogen. The mixture was allowed to warm to room temperature and stirring continued for 12 h. The reaction flask was cooled in an ice-bath, and water (10 mL) was slowly added under stirring. The layers were separated, the water layer was extracted three times with ether, and the combined ether solutions were dried with $MgSO_4$. After removal of the solvent the oily residue was purified by column chromatography (silica, petroleum ether) and afforded 1-bromo-8-chlorotetracyclo-[4.3.0.0^{2,8}.0^{4,7}]nonane (**15a**) (1.07 g, 46%, R_F = 0.63) and 1-bromo-8-methyltetracyclo[4.3.0.0^{2,8}.0^{4,7}]nonane (**15b**) (0.187 g, 9%, R_F = 0.69), both as colorless liquids.

15a: IR (film): $\tilde{\nu}$ 2999, 2961, 2931, 2857, 1263, 1245, 1225, 1195, 1166, 1035, 1022, 992, 972, 911, 901, 888, 839, 799, 625, 601 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.34 (d, $^2J_{HH}$ = 11.1 Hz, 1 H, 5-H_{endo}), 1.82 (d, $^2J_{HH}$ = 13.2 Hz, 1 H, 3-H), 1.97 (dm, $^2J_{HH}$ = 13.2 Hz, 1 H, 3-H), 2.08 (dm, $^2J_{HH}$ = 11.1 Hz, 1 H, 5-H_{exo}), 2.36, 2.40 (AB system, $^2J_{HH}$ = 6.8 Hz, 2 H, 9-H_2), 2.73 (m, 1 H, 6-H), 2.83 (m, 2 H, 2-, 4-H), 3.05 (m, 1 H, 7-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.14 (t, C-5), 33.45 (t, C-3), 39.17 (d, C-4), 48.10 (d, C-6), 51.84 (t, C-9), 53.22 (d, C-7), 53.65 (s, C-1), 65.13 (s, C-8), 65.50 (d, C-2). MS (70 eV, EI): *m*/*z* (%) 199 (5), 197 (6, M^+ − Cl), 155 (12), 153 (37, M^+ − Br), 117 (86), 115 (44), 102 (35), 100 (100), 91 (34). $C_9H_{10}BrCl$ (233.54): calcd C 46.29, H 4.32; found C 46.51, H 4.19.

15b: IR (film): $\tilde{\nu}$ 2952, 2924, 2884, 2857, 1452, 1315, 1234, 1206, 1186, 1165, 1115, 1071, 1050, 1036, 1027, 999, 979, 924, 895, 862, 668, 601 cm^{-1}.-^1H NMR (300 MHz, $CDCl_3$): δ 1.09 (s, 3 H, Me), 1.29 (d, $^2J_{HH}$ = 11.3 Hz, 1 H, 5-H_{endo}), 1.70 (m, 2 H, 3-H_2), 1.93 (s, 2 H, 9-H_2), 2.02 (dt, $^2J_{HH}$ = 11.3 Hz, 1 H, 5-H_{exo}), 2.40 (m, 1 H, 2-H), 2.72 (m, 3 H, 4-, 6-, 7-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.43 (q, C-10), 27.73 (t, C-5), 33.74 (t, C-3), 39.00 (d, C-4), 47.03 (d, C-6), 49.71 (s, C-1), 49.77 (t, C-9), 51.13 (d, C-7), 59.32 (s, C-8), 62.58 (d, C-2). MS (70 eV, EI): *m*/*z* (%) 133 (100, M^+ − Br), 105 (43), 93 (12), 91 (64), 80 (90), 79 (33). $C_{10}H_{13}Br$ (213.12): calcd C 56.36, H 6.15, Br 37.49; found C 56.37, H 6.19, Br 37.18.

(b) 11a and MeLi/LiBr: **11a** (3.04 g, 10.0 mmol) and a solution of MeLi/LiBr (51.1 mmol) in ether were allowed to react as described above. The same workup procedure afforded after column chromatography of the oily organic residue in the first fraction a 1:1 mixture of **15a** and 1,8-dibromotetracyclo[4.3.0.0^{2,8}.0^{4,7}]nonane (**15c**) (1.06 g, 41%) and in the second fraction **15b** (165 mg, 8%). **15c** was obtained pure as a colorless oil by preparative GC (oven 160 °C; helium flow 40 mL/min; retention time: **15a**, 25.7 min; **15c**, 35.1 min).

15c: IR (film): $\tilde{\nu}$ 2999, 2962, 2931, 2857, 1263, 1246, 1227, 1197, 1165, 1105, 1074, 1052, 1034, 1023, 1009, 993, 974, 917, 906, 890, 844, 634, 618, 601 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.30 (d, $^2J_{HH}$ = 11.3 Hz, 1 H, 5-H_{endo}), 1.79 (d, $^2J_{HH}$ = 13.6 Hz, 1 H, 3-H), 1.98 (dm, $^2J_{HH}$ = 13.6 Hz, 1 H, 3-H), 2.05 (dm, $^2J_{HH}$ = 11.3 Hz, 1 H, 5-H_{exo}), 2.39, 2.46 (AB system, $^2J_{HH}$ = 7.6 Hz, 2 H, 9-H_2), 2.70 (m, 1 H, 6-H), 2.83 (m, 1 H, 4-H), 2.88 (m, 1 H, 2-H), 3.13 (m, 1 H, 7-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.06 (t, C-5), 33.36 (t, C-3), 39.26 (d, C-4), 47.96 (d, C-6), 52.54 (t, C-9), 54.09, 54.61 (2 s, C-1, C-8), 54.31 (d, C-7), 66.01 (d, C-2). MS (70 eV, EI): *m*/*z* (%) 199 (26), 197 (26, M^+ − Br), 146 (32), 144 (35), 118 (41), 117 (100), 115 (32), 91 (28), 77 (13), 65 (19). $C_9H_{10}Br_2$ (277.99): calcd C 38.89, H 3.63; found C 39.28, H 3.52.

(c) 11b and MeLi, salt-free: **11b** (0.440 g, 1.01 mmol) and a solution of MeLi, salt-free (5.0 mL of a 1.6 M solution, 8.0 mmol) in ether were allowed to react as described above. The same workup procedure afforded **15c** (151 mg, 54%) as a colorless oil, whose NMR spectrum showed also a trace of **15b**.

(d) 11d and sodium bis(trimethylsilyl)amide (14): **11d** (0.920 g, 3.41 mmol) in ether (7.0 mL) was added dropwise under stirring to a solution of **14** (8.5 mmol) in THF (8.5 mL) which was kept in an ice bath. Stirring was continued for 12 h at room temperature. After aqueous workup, the residual oil of the organic fraction was flash-chromatographed and distilled, giving **15a** (0.510 g, 64%) as a colorless oil of bp 20−25 °C/0.001 mbar.

(e) 11e and sodium bis(trimethylsilyl)amide (14): **11e** (0.450 g, 1.42 mmol) in 5 mL ether was added dropwise under stirring to **14** (3.0 mmol in 3.0 mL of THF), cooled in an ice bath. After a reaction time of 12 h at room temperature, aqueous workup and purification of the residual oil by column chromatography afforded 1-iodo-8-chlorotetracyclo[4.3.0.0^{2,8}.0^{4,7}]nonane (**15d**, 230 mg, 58%) as a pale yellow oil.

15d: IR (film): $\tilde{\nu}$ 3069, 2999, 2938, 2922, 2852, 1475, 1431, 1188, 1176, 1120, 1089, 1029, 997, 862, 800, 759, 743, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (d, $^2J_{HH}$ = 11.2 Hz, 1 H, 5-H_{endo}), 1.72 (d, $^2J_{HH}$ = 13.7 Hz, 1 H, 3-H), 1.89 (dm, $^2J_{HH}$ = 13.7 Hz, 1 H, 3-H), 2.08 (dm, $^2J_{HH}$ = 11.2 Hz, 1 H, 5-H_{exo}), 2.38, 2.47 (AB system, $^2J_{HH}$ = 6.8 Hz, 2 H, 9-H_2), 2.73−2.88 (m, 4 H, 2-, 4-, 6-, 7-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.60 (s, C-1), 28.59 (t, C-5), 33.75 (t, C-3), 39.09 (d, C-4), 50.29 (d, C-6), 51.48 (d, C-7), 53.48 (t, C-9), 66.74 (d, C-2), 67.10 (s, C-8). MS (70 eV, EI): *m*/*z* (%) 282 (1), 280 (4, M^+), 153 (22), 127 (41), 125 (86), 118 (16), 117 (94), 116 (16), 115 (72), 102

(27), 100 (68), 91 (54), 78 (15), 77 (33). $C_9H_{10}ClI$ (280.54): calcd C 38.53, H 3.59; found C 38.73, H 3.60.

In a second experiment carried out as described above with **11e** (1.80 g, 5.68 mmol) and **14** (14.0 mmol), 1.16 g (73%) of **15d** was isolated.

(f) 11f and sodium bis(trimethylsilyl)amide (14): A solution of **11f** (3.60 g, 10.0 mmol) in ether (100 mL) was added dropwise to a stirred solution of **14** (25.0 mmol) in THF (25 mL), which was kept in an ice bath. Stirring was continue for 12 h. Aqueous workup afforded oily **15c** (2.71 g, 97%), whose ^{1}H NMR spectrum did not show any impurities. Distillation at 35 °C (bath)/2.0×10^{-5} mbar gave **15c** (2.44 g, 88%) as a colorless liquid.

(g) Tetracyclo[4.3.0.0^{2,8}.0^{4,7}]nonane (**15e**): Dibromide **15c** (1.39 g, 5.00 mmol), tri-*n*-butyltinhydride (3.25 g, 11.2 mmol), and a trace of azobisisobutyronitrile were irradiated in a quartz vessel for 8 h at room temperature ($\lambda \geq 356$ nm). Careful distillation afforded **15e** (433 mg, 72%) as a colorless liquid, bp 70 °C/12 mbar.

15e: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (d, $^2J_{HH} = 7.1$ Hz, 1 H, 5-H$_{endo}$), 1.10 (d, $^2J_{HH} = 10.5$ Hz, 1 H, 3-H), 1.45 (d, $^2J_{HH} = 12.2$ Hz, 1 H, 9-H), 1.55 (dm, $^2J_{HH} = 12.2$ Hz, 1 H, 9-H), 1.72 (dm, $^2J_{HH} = 7.1$ Hz, 1 H, 5-H$_{exo}$), 2.08 (dm, $^2J_{HH} = 10.5$ Hz, 1 H, 3-H), 2.24 (m, 1 H, 4-H), 2.36−2.42 (m, 2 H, 1-, 8-H), 2.53 (m, 1 H, 2-H), 2.58 (m, 1 H, 6-H), 2.91 (m, 1 H, 7-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.07 (t, C-5), 34.60 (t, C-3), 37.86 (d, C-6), 38.04 (t, C-9), 40.23 (d, C-4), 44.18 (d, C-7), 45.32, 46.07 (2 d, C-1, C-8), 49.60 (d, C-2). MS (70 eV, EI): *m*/*z* (%) 119 (1, M$^+$ − H), 91 (37), 79 (49), 77 (27), 66 (100). C_9H_{12} (120.19): calcd C 89.94, H 10.06; found C 89.25, H 10.36.

In a second identical experiment the irradiation time was only 4 h. Besides **15e**, the distillate contained a 3:2 mixture of monobromides **15f** and **15g**. This mixture was separated from **15e** by preparative GC, but could not be segregated into the pure components.

15f: ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.76 (t, C-5), 35.30 (t, C-3), 39.62, 40.73, 41.40 (3 d, C-1, C-4, C-6), 44.21 (t, C-9), 52.01 (d, C-7), 57.07 (d, C-2), 61.60 (s, C-8).

15g: ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.04 (t, C-5), 35.49 (t, C-3), 39.48 (d, C-4), 42.18 (d, C-8), 43.98 (t, C-9), 44.09 (d, C-7), 46.82 (d, C-6), 59.26 (d, C-2), 60.76 (s, C-1).

15f/g: $C_9H_{11}Br$ (199.09): calcd C 54.30, H 5.57, Br 40.13; found C 54.31, H 5.33, Br 40.60.

Reaction of 11 with Strong Bases in the Presence of Further Trapping Reagents. (a) 11a and MeLi/LiBr in the presence of cyclohexene or tetramethylethylene: To **11a** (1.52 g, 4.99 mmol), dissolved in 100 mL of a 1:1 mixture of ether and cyclohexene or tetramethylethylene and cooled in a dry ice bath was added dropwise under stirring a solution of MeLi (5.44 mmol) in ether. Stirring was continued for 12 h at room temperature. Aqueous workup of both experiments afforded an oily product, whose NMR spectrum showed only signals of **11a**, and **15a**, **15b**, and **15c**.

(b) 11a and MeLi, salt-free, in the presence of α-methylstyrene: To a solution of **11a** (1.10 g, 3.61 mmol) and α-methylstyrene (50 mL) in ether (200 mL), cooled in a dry ice bath, was added dropwise with stirring a solution of MeLi (salt-free, 4.00 mmol) in ether (75 mL) and α-methylstyrene (25 mL). Stirring was continued for 12 h at room temperature. Aqueous workup afforded in the organic fraction a slightly orange liquid, whose volatile parts were removed at 25 °C (bath) and a vacuum up to 2.0×10^{-5} mbar. The remaining oil was purified by column chromatography (kieselgel, petroleum ether) leading to a 1:1 mixture of 1-bromo-8-chloro-7-(2-phenyl-2-propen-l-yl)tricyclo-[4.3.0.0^{2,7}]nonane (**16**) and 1-bromo-7-chloro-8-(2-phenyl-2-propen-1-yl)tricyclo[4.3.0.0^{2,8}]nonane (**17**) (80 mg, 6%).

In a second experiment, 8.85 g (29.1 mmol) of **11a** were reacted with 1.11 equiv of MeLi and α-methylstyrene and the workup procedure was carried out as described above. Besides **16** and **17**, the NMR spectrum of the crude oily product indicated the additional formation of the stereoisomeric 1-bromo-7-(1-chloro-2-phenyl-2-methylcyclopropyl)-tricyclo[4.2.0.0^{2,7}]octanes **18** and **19**. Column chromatography afforded in the first fraction **19** (160 mg, 1.6%). Obviously, **19** did not survive column chromatography. In the second fraction a mixture of **16** and **17** (419 mg, 4%) was obtained, which was contaminated by a small amount of a third compound of unknown structure. This mixture was subjected to a HPLC separation, which afforded 20 mg of **16**, still contaminated by a side-product, and 20 mg of pure **17**.

16: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40−1.75, 1.86−2.08 (2 m, 7 H, 6-H, 3-, 4-, 5-H$_2$), 2.17, 2.52 (2 m, 2 H, 9-H$_2$), 2.53 (m, 1 H, 2-H), 2.88, 2.96 (2 d, $^2J_{HH} = 14.8$ Hz, 2 H, 3'-H$_2$), 4.09 (dd, $^3J_{HH} = 8.3$ Hz, $^3J_{HH} = 2.3$ Hz, 1 H, 8-H), 5.19 (s, 2 H, 1'-H$_2$), 7.20−7.46 (m, 5 H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.23 (t, C-4), 19.62, 20.39 (2 t, C-3, C-5), 32.42 (t, C-3'), 47.56 (t, C-9), 51.18 (d, C-2), 53.21 (s, C-1), 53.32 (d, C-6), 61.10 (s, C-7), 61.45 (d, C-8), 116.34 (t, C-1'), 126.61, 128.17 (2 d, aromatic C), 127.55 (d, aromatic C), 142.46 (s, C-2'), 145.32 (s, aromatic C). The assigment of the NMR signals is based on ^{1}H,^{1}H COSY and ^{1}H,^{13}C HETCOR spectra. GC MS (70 eV, EI): *m*/*z* (%) 317 (2), 315 (2, M$^+$ − Cl), 273 (10), 271 (32, M$^+$ − Br), 236 (20), 235 (100), 193 (19), 155 (25), 153 (46), 131 (34), 119 (24), 118 (20), 117 (77), 115 (33), 105 (56), 103 (21), 91 (51), 77 (20). $^{12}C_{18}{}^1H_{20}{}^{79}Br^{35}Cl$: calcd 350.0437, found 350.0480 (HR−MS). $^{12}C_{18}{}^1H_{20}{}^{35}Cl$: calcd 271.1253, found 271.1234 (HR−MS).

17: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92, 1.18−1.48, 1.72 (3 m, 6 H, 3-, 4-, 5-H$_2$), 1.62, 2.40 (2 m, 2 H, 9-H$_2$), 1.93, 2.47 (2 m, 2 H, 2-H, 6-H), 2.88, 2.95 (2 d, $^2J_{HH} = 13.9$ Hz, 2 H, 3'-H$_2$), 4.14 (s, 1 H, 7-H), 5.12, 5.39 (2 s, 2 H, 1'-H$_2$), 7.22−7.52 (m, 5 H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.15, 19.34, 21.41 (3 t, C-3, C-4, C-5), 35.10 (t, C-3'), 48.82 (t, C-9), 52.39, 54.36 (2 d, C-2, C-6), 54.29 (s, C-1), 57.22 (s, C-8), 63.56 (d, C-7), 115.79 (t, C-1'), 126.12, 128.45 (2 d, aromatic C), 127.81 (d, aromatic C), 140.77 (s, C-2'), 144.76 (s, aromatic C). The assigment of the NMR signals is based on ^{1}H,^{1}H COSY and ^{1}H,^{13}C HETCOR spectra. GC MS (70 eV, EI): *m*/*z* (%) 352 (2), 350 (2, M$^+$), 317 (5), 315 (5), 273 (22), 271 (63), 236 (20), 235 (100), 193 (15), 167 (21), 155 (37), 153 (78), 141 (15), 131 (31), 129 (19), 117 (47), 115 (28), 103 (25), 91 (49), 77 (23). $^{12}C_{18}{}^1H_{20}{}^{79}Br^{35}Cl$: calcd 350.0437, found 350.0361 (HR−MS); $^{12}C_{18}{}^1H_{20}{}^{35}Cl$: calcd 271.1253, found 271.1249 (HR−MS).

18: ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.99, 19.20, 19.48 (3 t, C-3, C-4, C-5), 25.59 (t, C-3'), 26.00 (q, C-4'), 32.21 (s, C-2'), 44.99, 46.62, 50.86 (3 s, C-1, C-1', C-7), 53.28 (t, C-8), 62.63, 65.36 (2 d, C-2, C-6), 126.09 (d, aromatic C 127.16, 128.21 (2 d, aromatic C), 141.17 (s, aromatic C).

19: IR (film): $\tilde{\nu}$ 3026, 2994, 2943, 2903, 2873, 2852, 1495, 1462, 1444, 1429, 1265, 1180, 1095, 1067, 1041, 1026, 943, 927, 884, 766, 699, 678, 664 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (d, $^2J = 6.4$ Hz, 1 H, 3'-H), 1.48 (s, 3 H, 4'-H$_3$), 1.61 (d, $^2J = 6.4$ Hz, 1 H, 3'-H), 1.58−1.93 (m, 6 H, 3-, 4-, 5-H$_2$), 2.24, 2.29 (AB system, $^2J = 2.3$ Hz, 2 H, 8-H$_2$), 2.63, 2.83 (2 m, 2 H, 2-H, 6-H), 7.22 (m, 5 H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.84, 19.63, 19.95 (3 t, C-3, C-4, C-5), 24.57 (q, C-4'), 27.66 (t, C-3'), 34.37 (s, C-2'), 44.51, 46.77, 49.72 (3 s, C-1, C-1', C-7), 54.54 (t, C-8), 64.58, 66.29 (2 d, C-2, C-6), 126.63 (d, aromatic C), 128.13, 128.58 (2 d, aromatic C), 143.26 (s, aromatic C). MS (70 eV, EI): *m*/*z* (%) 271 (1, M$^+$ − Br), 236 (1), 235 (2), 141 (15), 129 (12), 115 (14), 106 (11), 105 (100), 103 (16), 91 (44), 79 (25), 78 (13), 77 (36). $C_{18}H_{20}BrCl$ (351.71): calcd C 61.47, H 5.73; found C 61.10, H 5.45.

Reaction of 15c and 15d with *tert*-Butyllithium. (a) 15c and *t*-BuLi: To **15c** (530 mg, 1.91 mmol) in ether (10 mL) at −78 °C was added with stirring under nitrogen a solution of *t*-BuLi in pentane (6.29 mmol, 3.70 mL of a 1.7 M solution). The mixture was stirred for 12 h at room temperature. Aqueous workup followed by distillation of the oily organic residue gave a 1.7:1 mixture of 8-*tert*-butyltetracyclo-[4.3.0.0^{2,8}.0^{4,7}]nonane **25a** and 1-*tert*-butyltetracyclo[4.3.0.0^{2,8}.0^{4,7}]-nonane (**25b**) (180 mg, 53%) as a colorless liquid, bp 60 °C (bath)/10^{-3} mbar. Preparative GC allowed a partial separation of the isomers, giving two mixtures (6:1 and 0.66:1), whose NMR spectra could be assigned to the structures **25a** and **25b**.

25a: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (s, 9 H, Me), 1.03 (d, 1 H, 5-H$_{endo}$), 1.17 (d, 1 H, 3-H), 1.46 (d, 1 H, 9-H), 1.54 (m, 1 H, 9-H), 1.79 (m, 1 H, 5-H$_{exo}$), 2.06 (m, 1 H, 3-H), 2.25, 2.32, 2.39 (3 m, 3 H, 1-, 2-, 4-H), 2.58 (m, 1 H, 6-H), 2.78 (m, 1 H, 7-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.52 (q, C(*C*H$_3$)$_3$), 30.45 (t, C-5), 34.70 (t, C-3), 37.61 (t, C-9), 40.92, 40.97, 41.13 (3 d, C-1, C-4, C-6), 46.11 (d, C-7), 49.56 (d, C-2). The signals of the quartary C atoms could not be determined with certainty. GC-MS (70 eV, CI): *m*/*z* (%) 176 (2, M$^+$), 175 (4), 135 (16), 133 (18), 121 (100), 119 (48), 107 (51), 105 (30).

25b: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (s, 9 H, Me), 0.96 (d, 1 H, 5-H$_{endo}$), 1.14 (d, 1 H, 3-H), 1.41 (d, 1 H, 9-H), 1.54 (m, 1 H, 9-H),

1.60 (m, 1 H, 5-H_{exo}), 2.04 (m, 1 H, 3-H), 2.24 (m, 1 H, 2-H), 2.31 (m, 1 H, 4-H), 2.40 (m, 1 H, 8-H), 2.49 (m, 1 H, 6-H), 3.00 (m, 1 H, 7-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.09 (q, C(CH_3)$_3$), 30.00 (t, C-5), 34.47 (t, C-3), 37.46 (t, C-9), 38.69, 39.77, 41.00 (3 d, C-4, C-6, C-8), 48.75 (d, C-7), 49.17 (d, C-2). The signals of the quartary C atoms could not be determined with certainty. GC-MS (70 eV, CI): *m*/*z* (%) 176 (2, M^+), 175 (6), 133 (23), 122 (29), 121 (45), 119 (40), 108 (27), 107 (100), 105 (36). **25a/b** $C_{13}H_{20}$ (176.30): calcd C 88.57, H 11.43; found C 88.45, H 11.58.

(b) 15d and *t*-BuLi: **15d** (673 mg, 2.40 mmol) and *t*-BuLi (7.31 mmol, 4.30 mL of a 1.7 M solution in pentane) were allowed to react as described above and afforded a 1.65:1 mixture of **25a** and **25b**.

In a series of further experiments, **15c** or **15d** was reacted with *t*-BuLi and the product ratio **25a**/**25b** determined by analytical GC with a capillary column, which separated **25a** and **25b** completely. All reactions were carried out with 200 mg (0.720 mmol) of **25a** or **25b** and 2.21 mmol of *t*-BuLi in 5.0 mL of ether at −78 °C under nitrogen with stirring. After 12 h of stirring at 20 °C water was added at 0 °C, the phases separated, the ether layer dried with $MgSO_4$, the ether solution directly injected into the vpc, and the peak areas of **25a** and **25b** computer integrated. For each run, five injections were recorded; the reproducibility was 0.5%. The results are given in Table 5. Within the error limits, the product ratios of both series of experiments are identical.

Table 5. **25a/25b** Ratios from **15c** and **15d** with *t*-BuLi

compd	run no.	**25a/25b**	compd	run no.	**25a/25b**
15c	1	1.69	**15d**	1	1.63
	2	1.72		2	1.65
	3	1.77		3	1.70
	4	1.75		4	1.68
		1.73 ± 0.05			1.66 ± 0.05

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