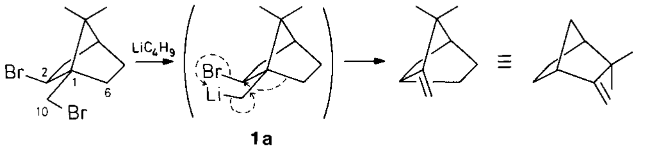
An Unprecedented Elimination-Driven Migration: The Reductive Dihalobornane–Camphene Rearrangement**

László Garamszegi and Manfred Schlosser*

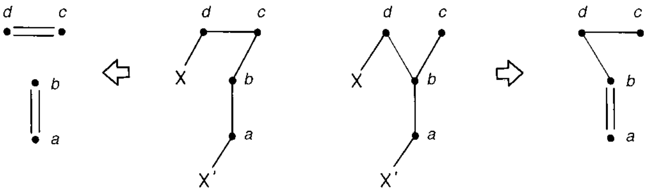
The concept of the "variable transition state" of β-eliminations,[1] viewed as a mechanistic continuum stretching from E1(C^+) to E1cb, has fascinated generations of chemists and has profoundly shaped their reasoning. The fundamental idea, that not only ground states but also transition states can be conceived as resonance hybrids resulting from the superposition of two or more limiting structures, has later been extended with remarkable success to cycloaddition reactions,[2, 3] in particular for the rationalization of their ease and regioselectivity. Here we demonstrate that even complex elimination processes which involve the breaking and making of several bonds can be brought about in a highly concerted fashion under variable push–pull control. Similar conclusions have been previously drawn for fragmentation reactions on the basis of stereoelectronic criteria.[4]

In relation with recent work in the field of selective structural manipulations of monoterpenes,[5] we have observed the quantitative conversion of *exo*-2,10-dibromobornane into camphene upon treatment with butyllithium in tetrahydrofuran (or diethyl ether). This result can be plausibly explained by assuming that a halogen–metal exchange occurs at the 10- rather than the 2-position, thus generating the less basic *exo*-2-bromo-10-bornyllithium (**1a**; Scheme 1). This species would have to rearrange instantaneously under loss of lithium bromide to afford camphene.



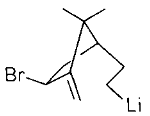
Scheme 1. Conversion of *exo*-2,10-dibromobornane into camphene upon treatment with butyllithium by halogen–metal permutation.

This migration–elimination mode differs from a classical heterolytic fragmentation[4] in essentially one respect. Since carbon atoms 2 and 6 (centers *d* and *c* in Scheme 2) are not yet connected at the stage of the intermediate **1a**, they will ultimately be linked by only a single rather than a double bond. The bond between carbon atoms 1 and 2 (centers *b* and *d*) is formally irrelevant since it does not directly participate in the reaction event, but just ensures the proximity of the crucial structural entities (in particular, centers *c* and *d*).

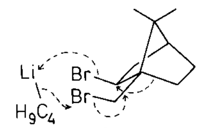


Scheme 2. Heterolytic fragmentation (left) and elimination–migration (right).

Other reaction patterns cannot be ruled out a priori, of course. Thus, a stepwise sequence consisting of the opening[6] of the cyclopentylmethyllithium subunit to produce a 5-hexenyllithium intermediate (**2a**) immediately followed by intramolecular, ring-closing nucleophilic (S_N2-type) attack could be well envisioned. Alternatively, a hyperconcerted simultaneous removal of both bromine atoms under the action of butyllithium may take place (transition state **3**). In the second case, the initially postulated intermediate **1a** would be bypassed. Trapping experiments should hence allow one to proceed to a first mechanistic selection.



2a



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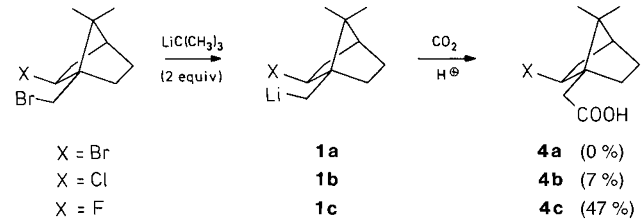
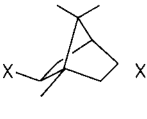
All attempts to characterize the presumptive intermediate **1a** by interception with dry ice or benzaldehyde failed, even at −125 °C. However, the corresponding chloro and fluoro analogues (**1b** and **1c**) could be trapped by carboxylation at −125 °C and −75 °C, respectively, affording the acids **4b** and **4c** in 7% and 47% yield (Scheme 3). About 25 °C above the temperatures at which they had been generated, species **2b** and **2c** were converted into camphene (33% and 48%, respectively) by an elimination–migration process.



Scheme 3. Evidence for intermediates **1** from trapping reactions.

In the chloro series, 2-chlorobornane (**5b**, ca. 30%), 2-chloro-7,7-dimethyl-1-(2,2-dimethylpropyl)bicyclo[2.2.1]heptane (**6b**, ca. 15%), 2,2-dimethyl-3-methylidenebicyclo[2.2.1]heptane (**8**, ca. 5%), and 10,10′-biscamphenyl (**9**, ca. 5%) were identified as by-products. In the fluoro series, 2-fluoro-7,7-dimethyl-1-(2,2-dimethylpropyl)bicyclo[2.2.1]heptane (**6c**, ca. 10%) and 10,10′-bis(2-fluorobornyl) (**7c**, ca. 30%) were detected.



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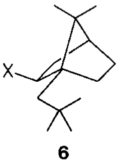

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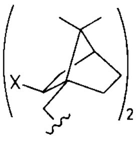

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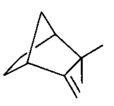

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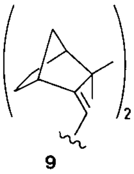

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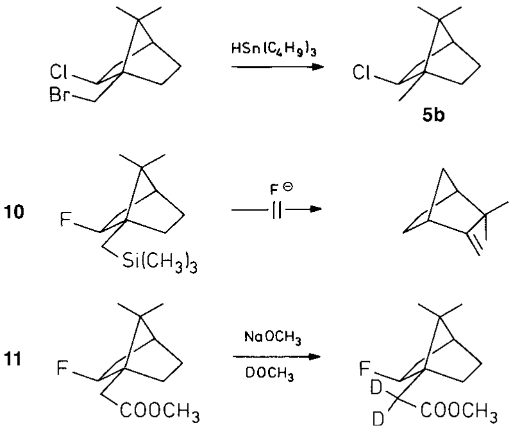
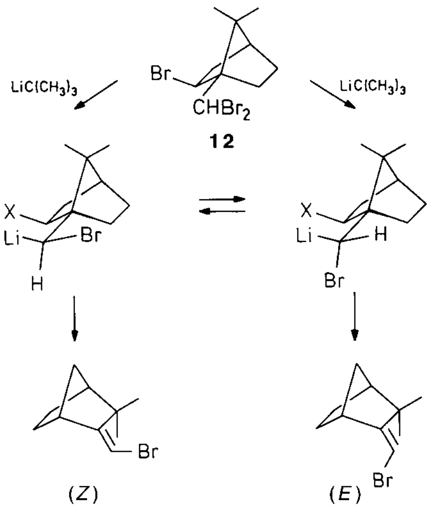
Further model reactions have been carried out to exclude remaining mechanistic options and thus, indirectly, to support the favored push–pull process. The rearrangement cannot be mediated by radicals since upon treatment of 10-bromo-2-chlorobornane with tributyltin hydride, 2-chlorobornane (**5b**) is obtained as the exclusive product (Scheme 4). It can neither be cationic[7]—in other words, Wagner–Meerwein-like—since 2-bromo-, 2-chloro-, and 2-fluoronorbornane are perfectly inert towards butyllithium in the presence or absence of solubilized lithium bromide. Finally, it cannot even be anionic since no halide elimination accompanied by rearrangement occurs when 2-fluoro-10-(trimethylsilyl)bornane is desilylated with tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) and methyl 2-fluoro-10-bornanecarboxylate is submitted to base-catalyzed hydrogen–deuterium exchange. The latter findings also argue against the intermediacy of ring-opened species such **2**, since the absence of a metal (lithium) should have no adverse effect on the rate of formation of the 2-halobornanide precursor (**1**, without metal) nor on the position of the equilibrium established between **1** and **2**.



Scheme 4. Exclusion of possible reaction mechanisms with model reactions.

The concerted push–pull elimination–migration process should be relatively insensitive to steric hindrance encountered in the final products. In accordance with this expectation, 2,10,10-tribromobornane (**12**) reacts with *tert*-butyllithium to give a *Z*/*E* mixture (2:3) of 10-bromocamphene in 69% yield, from which the pure *Z* isomer, a versatile building block,[5] can be isolated after kinetic separation.[5] The tribromo compound **12** can be readily prepared by addition of bromine to the *E* isomer[5] of 10-bromocamphene (Scheme 5).



Scheme 5. Insensitivity of the push–pull process to steric hindrance.

Numerous elimination-driven skeletal reorganizations are known, for example the Wagner–Meerwein, Fittig–Zincke (pinacolic), and Fritsch–Buttenberg–Wiechell rearrangements.[8] At first sight, they have mechanistically nothing in common with the present topic. In the same way, any coincidence between the 2,10-dihalobornane–camphene elimination–migration and the family of Lossen, Hofmann, and Curtius rearrangements[8] appears to be merely schematic, since all these latter reactions involve cationic intermediates. However, at least the solvolytic rearrangement of isoborneol esters must be supported by a push contribution, as it implies σ delocalization.[9, 10] Donor (e.g., trimethylstannylmethyl[11]) and acceptor substituents (e.g., cyano[12]) attached to the bridgehead C1 position indeed cause a pronounced rate enhancement or deceleration, respectively. Thus, we recognize the emerging of a new continuum of multibond reorganizing mechanisms. They simultaneously employ push (electrofugal) and pull (nucleofugal) actions in variable blends. Often one feature clearly predominates, but sometimes both are balanced in roughly equal proportions. The latter appears to be the case with the 2,10-dihalobornane–camphene rearrangement.

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The First Organobismuth Rings: $(RBi)_3$ and $(RBi)_4$, $R = (Me_3Si)_2CH$[**]

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Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

Monocyclic oligomers $(RE)_n$, R = organo group, $n = 3-6$, are only well known for the three central elements of the fifth main group (E = P, As, Sb). The existence of the corresponding organobismuth rings is questionable. Compounds such as $(PhBi)_x$,[1] and $(2,4,6\text{-}Ph_3C_6H_2Bi)_x$,[2] which are described in the literature are possibly rings but their structures have not been proven. The first fully characterized organobismuth(I) compound is a dibismuthene: $(RBi)_2$ ($R = 2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2$).[3]

Inorganic bismuth compounds have a tendency to form cyclic structures, for example, in the element bismuth, in polycyclic cations such as Bi_9^{5+}[4] and Bi_5^{3+},[5] and in bismutides such as Bi_4^{2-}.[6] Here we report the synthesis and the structure of the trimeric and tetrameric compounds **1** and **2**, the first organobismuth rings.

R_3Bi_3 R_4Bi_4 ($R = (Me_3Si)_2CH$)
1 **2**

Compounds **1** and **2** were synthesized by reduction of $RBiCl_2$[7] with magnesium filings in THF at −35 °C. In solution there is an equilibrium between the two organobismuth rings [Eq. (1)]. The equilibrium constant $K = [R_3Bi_3]^4/[R_4Bi_4]^3$ is $40 \pm 5\ mol\,L^{-1}$ in C_6D_6 at 23 °C. As

$$4\,R_3Bi_3 \rightleftharpoons 3\,R_4Bi_4 \qquad (1)$$

expected, the equilibrium is shifted in favor of the four-membered ring when the solution is cooled. Black crystals of **2** were grown from a solution in petroleum ether at low temperatures. When the crystals were dissolved in hydrocarbons fascinating color changes were observed: first the four-membered ring dissolved to give an intensive green solution. Within a few minutes the ring – ring equilibrium was established and the red color associated with the three-membered ring predominated in the solution. At low temperatures the fraction of **2** increased again and the solutions became first brown and then black on cooling. Both solutions of **1** and **2**, as well as the crystals of **2** are air-sensitive and thermolabile. In the absence of light and air, solutions in C_6D_6 decompose at ambient temperature with first-order kinetics to give R_3Bi[8] and bismuth. At 23 °C the concentrations of the rings decreased with half-life periods of 20.2 ± 2.0 h for **2** and 31.6 ± 2.7 h for **1**. At −28 °C the crystals of **2** and the solutions of **1** and **2** are stable for several months.

The structure of **1** can be derived from the NMR spectra. It is a tribismirane with $(Me_3Si)_2CH$ groups in *cis – trans* positions. The ^1H NMR spectrum shows singlets for the methine protons, with an intensity ratio 1:2. As a consequence of the diastereotopy at the substituents in the *cis* positions there are three signals of equal intensity for the methyl protons. The ^{13}C NMR spectrum contains three signals for the carbon atoms of the methyl groups and two broad signals for the carbon atoms of the methine groups. The line broadening is a consequence of the interactions with the quadrupole moment of the bismuth nucleus. Similar signal patterns are also found in the NMR spectra of the antimony analogue of **1**, which was recently characterized by X-ray crystallography.[9] The ^1H and ^{13}C NMR spectra of **2** in C_6D_6 show two signals each, corresponding to an *all-trans* arrangement of the alkyl substituents. To date **1** and **2** could not be characterized by mass spectrometry; even with soft ionization techniques only signals of decomposition products (R_3Bi, R_4Bi_2) could be identified. A single-crystal X-ray structure analysis for **2** confirmed the *all-trans* configuration of the tetrabismethane in the solid state (Figure 1).[10]

The structure contains a folded four-membered bismuth ring. The bismuth – bismuth bond lengths lie between 297.0(5) and 304.4(2) pm. Similar Bi – Bi bond lengths were also measured for dibismuthanes Ph_4Bi_2 (299.0(2)[11]) and $(Me_3Si)_4Bi_2$ (303.5(3)[12]). The anionic ring Bi_4^{2-} has slightly shorter bonds (293.6(2), 294.1(2) pm).[6] The double bond in the dibismuthene $[\{2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2Bi\}_2]$ (Bi – Bi 282.06(8) pm) is even shorter.[3] The Bi – C distances in **2** vary between 233(2) and 239(2) pm. They are a little longer on average than in R_3Bi ($R = (Me_3Si)_2CH$, Bi–C 230.6(13) – 234.7(13) pm).[8] The Bi-Bi-Bi bond angles in **2** lie between 78.97(8)and 79.93(6)°; in contrast the Bi-Bi-C angles are relative large (range between 93.9(6) and 109.5(5)°). The larger Bi–Bi distances and Bi-Bi-C angles may be related to repulsive interactions of the alkyl substituents in the mole-

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