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Metalation of 9-Oxabicyclo[3.3.1]nonadiene – the Deprotonation Path to Bridgehead Olefins

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A new route to bridgehead olefins based on a deprotonation reaction has been established. The deprotonation of 9-oxabicyclo[3.3.1]nonadiene (**1**) with *t*BuLi/TMEDA occurs selectively in the allylic position. Whilst **1** has four allyl positions, only one bridgehead proton was removed, as demonstrated by quenching with Me_3SnCl, Me_3SiOTf, and Me_3PbCl. With a threefold excess of deprotonating agent and subsequent treatment with Me_3SnCl, three stannylated derivatives – **3**, **4a**, and **4b** – were obtained. Compound **3** is the starting diene **1** substituted at the bridgehead position 1 in the skeleton, and when smaller quantities of deprotonating agent were used it was the only stannylated derivative of **1** formed. Compounds **4a** and **4b** had each undergone a shift of one double bond to give bridgehead olefins *exo*- and *endo*-stannylated at position 3 in the skeleton. The common intermediate precursor of compounds **3**, **4a**, and **4b** was a bridgehead allyl anion, which can also be generated from **3** and could be observed directly by ^{6}Li and ^{13}C NMR spectroscopy. After quenching of the anion with Me_3SiOTf, and Me_3PbCl, two silylated and plumbylated derivatives of **1** were obtained in each case: the bridgehead-substituted compounds and the 3-*exo*-substituted bridgehead olefins. The stannylated bridgehead olefins **4a** and **4b** rearranged slowly to give **3** in what is formally a 1,3-stannatropic shift reaction. The kinetics of the reactions are zero-order in **4a** and **4b**, respectively, pointing to intermediate light-promoted homolytic cleavage of the Sn–C bond and the formation of a tight radical pair.

Introduction

Direct metalation of C–H sites, mostly through deprotonation with organometallic bases, continues to be a key step for functionalizing molecules.[1] From the organometallic point of view, deprotonation is especially attractive when it occurs next to double bonds. In such cases, anionic many-electron donor ligands would result, and these are prone to form π complexes of transition metals. The reactivities of such anionic ligands depend strongly on whether the donor-electron sets are conjugated or split into at least two parts, as in the type-**A** compounds in Figure 1. Ferrocene analogues of type **B** with split-π-system ligands,[2] for instance, are much more reactive than the parent ferrocene.

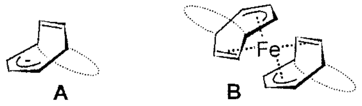

Figure 1. Split-π-system compounds.

For extension of the split donor-electron ligand concept one might think of starting from compounds of the general structure **C** (Figure 2), where E is an atom that has electron lone pairs available. Depending on the nature of E, the deprotonation of compound **C** may yield carbanions of type **D** or **E**, and subsequent treatment with electrophiles should result in a rich chemistry. Thus after quenching **D** with RX one would expect compounds **F** and **G**, while treatment with L_nM^+ [M = transition metal, e.g., Fe; L_n = ligand(s), e.g., cyclopentadienyl] would yield compounds of type **H**. Here the lone pair at atom E takes the place of the double bond in compound **A** and, together with the allyl fragment, the ligand features as an anionic six-electron donor/acceptor system. Compounds similar to **F**, **G**, and **H** have actually been found in the cases of the related bicyclo[3.2.1]-octadienyl, bicyclo[3.2.2]nonadienyl, and bicyclo[3.2.1]octenyl skeletons in which the bridge E is a CH_2[2,3] or a NCH_3 fragment.[4]

After quenching of **E** with RX, on the other hand, one would expect compounds **I** and **J**, while treatment with L_nM^+ should yield compounds of type **K**. The formation of the bridgehead-substituted derivatives **I** from **C** via **E** would be attractive, because it would avoid the preparation of the bridgehead halides commonly used for metal–halide exchange and subsequent treatment with nucleophiles. It would be also appealing to obtain **J** from **C** via **E**, as this would be a new general route to bridgehead olefins.[5]

Extension of the concept to double deprotonation of **C** and bridging of two L_nM^+ fragments by the resulting dianion **L** is also conceivable (Figure 2). In such a case two

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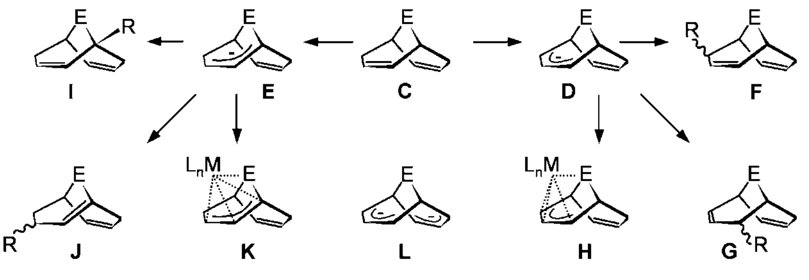


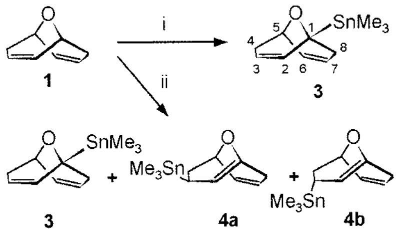
Figure 2. Deprotonation of compound **C** to yield carbanions of type **D** or **E**, and subsequent treatment with electrophiles.

lone pairs would be needed and E should be oxygen and the like. The ligand **L** with E = O has actually been claimed in a patent[6] to figure in Group 4 metal derivatives that catalyze the polymerization and copolymerization of ethylene, but no details are available. These various factors prompted us to study the direct metalation of 9-oxabicyclo[3.3.1]nona-2,6-diene[7] (**1**).

Results

Deprotonation and Stannylation

After recent synthetic improvements, the starting bicyclic ether **1** is available in multigram quantities.[8] Its treatment with organo-alkali metal bases turned out to be most efficient with *t*BuLi/TMEDA, and could be followed by the color change of the solution from colorless to yellow and orange. In order indirectly to establish the formation of some intermediate anion **2** (see Discussion), the reaction mixture was quenched with Me_3SnCl. As shown in Scheme 1, different stannylated derivatives of **1** were formed, depending on the stoichiometry and the temperature. Addition of one equivalent of *t*BuLi/TMEDA at –78 °C, stirring at –30 °C for four hours, a subsequent increase in the temperature to 25 °C for five minutes, and quenching with one equivalent of Me_3SnCl at –78 °C gave the bridgehead derivative **3**, while use of a more than threefold excess of the metalating agent under the same conditions additionally gave the stannyl derivatives **4a** and **4b**. Compound **3** was also obtained after deprotonation of **1** with *n*-BuLi/KO*t*Bu and quenching with Me_3SnCl, but the yield was lower.



Scheme 1. *i*) a *t*BuLi/TMEDA 1/1; b: Me_3SnCl. *ii*) a: *t*BuLi/TMEDA 3/1; b: Me_3SnCl.

Compound **3** was a white microcrystalline powder, whilst the mixtures of **3**, **4a**, and **4b** were colorless, oily liquids which gave identical molecular ions in GC/MS analyses after partly different retention times (t_Rs). Integration of GC runs of **3**, **4a**, and **4b** (showing two peaks) with different concentrations and comparison with the NMR spectra (showing three signal patterns; see below) showed that t_R was shortest for **3**, while **4a** and **4b** could not be resolved, a fact pointing to closely related isomers. We were not able to obtain **4a** and **4b** in crystalline form, so emphasis was laid on establishing their structures by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. As **4a** and **4b** rearrange to give **3** (see below), samples with varying ratios of the isomers up to spectroscopically (Figure S1, Supporting Information) almost pure **3** could be investigated, and so the ^1H and ^{13}C NMR signal patterns of **3**, **4a**, and **4b** could be identified. Three ^{119}Sn NMR signals appeared between –8 and –12 ppm, which is typical for Me_3Sn groups in allylic positions.[9] The compound with $\delta(^{119}Sn) = -11.6$ ppm gave nine ^{13}C NMR signals appearing in ranges known from **1**[8] and for Me_3Sn groups.[9] Two signals were found in the bridgehead carbon signal range, at $\delta = 72.6$ ppm and 66.2 ppm. The first signal showed $^1J(^{13}C,^1H)$ and $^1J(^{117/119}Sn,^{13}C)$ couplings of 148.2 Hz and 25.7 Hz, respectively, while the second signal had no one-bond C,H coupling and $^1J(^{117/119}Sn,^{13}C)$ couplings of 477.5 Hz and 499.8 Hz. Clearly, the last two values are one-bond Sn,C couplings, which indicated that 9-oxabicyclo[3.3.1]nona-2,6-diene (**1**) had been substituted in the bridgehead position to give **3**. In addition, the ^{13}C NMR signals were assigned by following the sequence of $^1J(^{13}C,^{13}C)$ couplings (Table S1), which correspond to what is known from the literature.[10] The $^1J(^{13}C,^1H)$ couplings are consistent with this assignment. The proton NMR spectrum of **3** features nine signals containing rich H,H coupling information; the most prominent values are listed in Table S1. The proton signal assignment was based on the characteristic shift ranges and on both the $^2J(^1H,^1H)$ and the $^3J(^1H,^1H)$ values. In particular, the three-bond couplings for the C-2, C-3, C-4 and the C-6, C-7, C-8 paths in **3** are significantly different, so that the two can be distinguished. Among the Sn,C couplings, those to C-3, C-5, and C-7 are most helpful. These are three-bond couplings, which profit from favorable dihedral angles and are thus bigger than those to C-2, C-4, C-6, and C-8. It is worth noting that the coupling across C-2 and C-8 is more efficient than that across the oxygen atom, although in the latter case the dihedral angle is close to optimal. No special effort to identify all expected $J(^{117/119}Sn,^1H)$ couplings was made.

The striking features of compounds **4a** and **4b** are their bridgehead double bonds. In the ^{13}C NMR spectrum each compound gives rise to four olefinic signals similar to those of **3** except for one (C-1), which is shifted to 154.8 and 161.1 ppm, respectively. The additional shift of up to about 40 ppm has contributions characteristic of olefinic bridgehead carbon atoms[11] and the effect of the oxo bridge.[12] While **3** has two signals in the range of aliphatic bridgehead carbon atoms (C-1/5, 65–75 ppm), **4a** and **4b** each have only one (C-5, slightly more shifted). Instead, **4a** and **4b** each show an additional signal in the methylene carbon atom range (C-3, 21.3 and 16.4 ppm) with Sn,C couplings (>360 Hz) showing that the Me_3Sn group is located at C-3. The suggested assignment of the signals of C-2, C-6, and C-7, as well as of C-4 and C-8, is based on the Sn,C couplings and on signal shift analogies. The two isomers **4a** and **4b** have rather similar NMR spectroscopic data with the notable exception of ^2J(Sn,C2) and ^3J(Sn,C-5). In particular, the three-bond Sn,C-5 coupling of **4a** is more than twice as small as that of **4b**. This establishes the *exo* and *endo* isomers, with unfavorable and favorable dihedral angles Sn, C-3, C-4, C-5 for **4a** and **4b**, respectively (for details see Figure S2). The structures of both compounds are further supported by the ^{1}H NMR spectroscopic data also given in the Experimental Section and in Table S1.

Rearrangement of the Bridgehead Olefins

When the NMR measurements on mixtures of the stannyl derivatives **3**, **4a**, and **4b** were repeated after some time it turned out that compounds **4a** and **4b** were not stable. For a more detailed study, time-dependent proton NMR spectra were recorded and the areas of the Me_3Sn signals were analyzed; Figure 3 shows that the content of **3** increased at the expense of those of **4a** and **4b**. When the measurements were started the mixture contained **3**, **4a**, and **4b** in the ratio of 10:68:22, while after 101 days it was 51:44:5. Data fits gave the rate constants in units of signal area per second $k(\mathbf{3}) = 5.0{\cdot}10^{-6}$, $k(\mathbf{4a}) = -2.7{\cdot}10^{-6}$, and $k(\mathbf{4b}) = -2.2{\cdot}10^{-6}$.

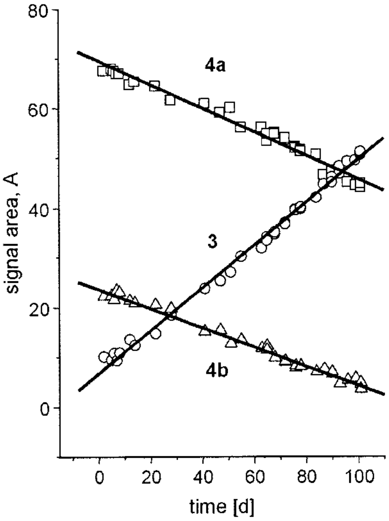
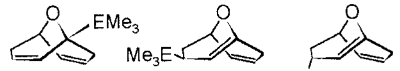


Figure 3. Time-dependent changes of the amounts of stannyl derivatives **3** (circles), **4a** (squares), and **4b** (triangles). The data are given as individual NMR signals scaled to the sum of the areas at a given time. The curves were obtained from data fits (see text).

Silyl and Plumbyl Derivatives

The deprotonated 9-oxabicyclo[3.3.1]nona-2,6-diene was also quenched with Me_3SiOTf and Me_3PbCl, in a reaction sequence similar to that shown in Scheme 1. In the case of the silyl derivatives the result was strongly dependent on the time during which the mixture was kept at ambient temperature after deprotonation. Restriction to 5 min, quenching, and work-up gave a mixture of two main products. Allowing the mixture to reach 25 °C overnight yielded a crude product consisting of many compounds, of which three were left after distillation. In both cases two resolved peaks appeared in the GC/MS runs, their mass spectra showing the same ions, albeit with different intensities. They were consistent with compounds **5** and **6a** (shown in Figure 4), established by NMR spectroscopy. There are also hints from the ^{13}C NMR spectra that the compound formed in addition after warming overnight is a coupling product of **1**, resulting from C,C bond formation between bridgehead carbon atoms. The t_R values of the silyl compounds are roughly 10% shorter than those of the stannyl compounds, a result that might be expected if the molecular weight difference determines their mobility in the GC column. No rearrangement was observed for compounds **6a**.



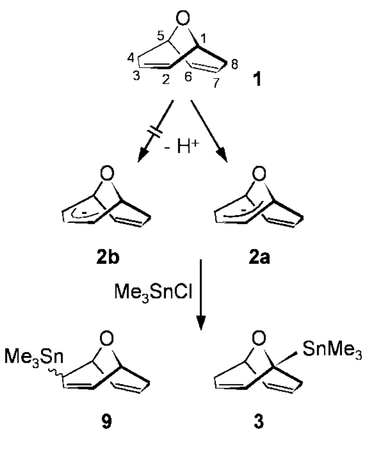
E = Si: **5** **6a**
E = Pb: **7** **8a** **8b**

Figure 4. Products of Me_3SiOTf and Me_3PbCl quenching.

In the case of the corresponding plumbyl compounds no meaningful GC/MS data were obtained from the oily liquids which resulted from low-temperature deprotonation, quenching, and work-up. However, these derivatives could be established by NMR spectroscopy. The spectra analysis of both the silyl and the plumbyl compounds was facilitated by the typical signals of the 5-H bridgehead atoms of the stannyl derivatives **3**, **4a**, and **4b** (4.2–4.9 ppm). In addition, **4a** and **4b** featured characteristic[13] doublets for 2-H between 5.7 and 6.0 ppm, with strongly split multiplets appearing for all other olefinic protons close to those doublets; the corresponding doublets and bridgehead proton signals were found for the silyl and plumbyl compounds, which was good evidence for molecules **5** and **6a** as well as **7** and **8a**, respectively (Figure 4). Many other multiplets of the proton signals were so characteristic that they could also be assigned by analogy to the stannyl derivatives. These data, together with the available ^{13}C NMR results and the couplings with ^{29}Si and ^{207}Pb, are collected in the Experimental Section and Table S2. As Si,H and Si,C coupling constants are much smaller than those with $^{119/117}$Sn and ^{207}Pb[14] the ^{29}Si satellites could not be resolved in some cases. In addition, the results were checked by $^1H,^{13}C$ HMQC NMR spectroscopy. Besides the plumbyl derivatives **7** and **8a**, the ^1H NMR spectrum showed characteristic signals of a second bridgehead olefin derivative, which is suggested to be **8b** [δ = 6.01 ppm, ^3J(2-H,3-H) = 11.0, ^4J(2-H,4-H*exo*) = 3.7 Hz, 2-H; 3.85 ppm, 5-H]. The ratio of the compounds **7**, **8a**, and **8b** derived from integration of these signals is 1:1:0.2, so the remaining small signals of **8b** were masked by those of **7** and **8a**. The NMR spectra further showed that the bridgehead olefins **8a** and **8b** rearrange to the bridgehead-substituted derivative **7**. So far, we have not been able to detect metalated derivatives of **1** with a silyl substituent in the *endo*-3 position.

Discussion

Several factors have to be considered for the deprotonation site of 9-oxabicyclo[3.3.1]nona-2,6-diene (**1**). The conventional hydrocarbon acidities[15] suggest that allylic protons should react first. In **1** the allylic protons 1/5-H should be less reactive than 4/8-H, because the resulting carbanion would suffer from a reduced interaction between the necessarily pyramidal C-1 (or C-5) and the adjacent double bond; the acidity of the corresponding benzylic protons in triptycene is strongly reduced.[16] On the other hand, the reactivity of 4-H (or 8-H) of **1** should also be reduced owing to the fact that the C-2, C-3, C-4 angle is smaller than in an ideal propene fragment.[17] Another important factor is the activation of the bridgehead protons by the neighboring oxygen atom. While things look complicated, the result is simple: the bridgehead-substituted stannyl derivative **3** is the final product after deprotonation of **1**, quenching with Me_3SnCl, and prolonged standing (Scheme 2). When **1** was treated with *n*-BuLi/TMEDA, *t*BuLi/TMEDA, *n*-BuLi/KO*t*Bu, *n*-BuLi/NaO*t*Bu, *t*BuLi, KO*t*Bu, lithium wire, or potassium (and quenched as described under Procedure A in the Experimental Section) neither of the two isomers of **9** (Scheme 2) and no doubly stannylated derivative (originating from species **L** in Figure 2) could be detected in the mixture. The deprotonation of **1** is therefore remarkably selective and gives the anion **2a**.



Scheme 2.

An independent route to **2a** is the cleavage of the Sn–C bond of compound **3** with *n*-BuLi. When this experiment was carried out in a NMR tube, new ^{13}C NMR signals consistent with the formation of **2a** were observed. The signals assigned to the double bond (C-6/7; δ = 123.1 and 130.6 ppm) and the bridgehead carbon C-5 (δ = 66.7 ppm) were very similar to the corresponding signals of the parent compound **1** (δ = 122.6, 130.1, and 66.3 ppm, respectively),[8] the allyl fragment C-1, C-2, C-3 showed up at 75.5, 128.9, and 63.9 ppm, respectively, while the signal assignment of C-4 and C-8 was hampered by the signals of the solvents, the reagent, and the byproducts. Carrying out the experiment with *n*-Bu^{6}Li gave a new ^6Li NMR signal at δ = –0.3 ppm, which corresponds to the signal shifts of other allyllithium derivatives.[18]

The ^{13}C signal pattern of the C-1, C-2, C-3 fragment of **2a** is similar to those of the allyl fragments of bicyclo[3.2.1]-octa-2,6-dienyl anion and bicyclo[3.2.2]nona-2,6-trienyl anion[19] and reflects the localization of negative charge at C-1 and C-3. As can be seen in Figure 5, this fits with the HOMO of **2a**, which has the largest coefficients at C-1 and C-3. Comparison of the orbitals π1, π2, and π3 of **2a** reveals that, on the one hand, the orbital contributions of the C-1, C-2, C-3 fragment are similar to the π orbitals of the allyl anion. On the other hand, because of the structure-induced orbital mixing, the MO contributions at C-1, C-2, and C-3 are no longer oriented parallel as in the parent allyl anion, so **2a** represents a bridgehead allyl anion featuring a strongly distorted π system. The distortion may be described by partial rotation of a CH_2 group of the parent allyl anion out of the C, C, C plane. In a detailed study[20] it has been shown that the rotation destabilizes the anion by 23 kcal·mol^{-1} (for the inward rotation corresponding to the situation at C-1 of **2a**) and that the engaged terminal C atom undergoes pyramidalization.

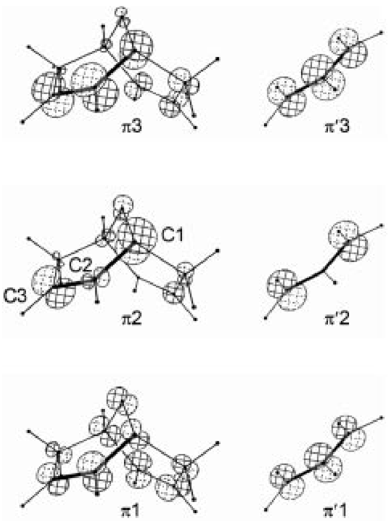
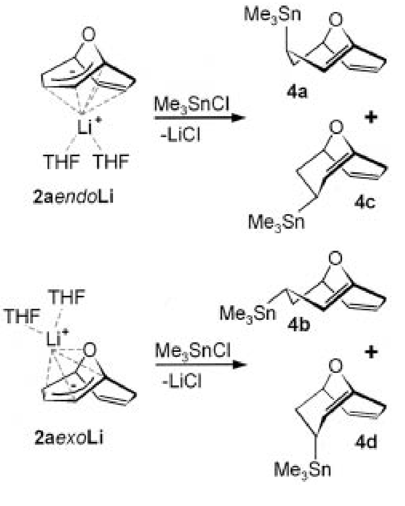


Figure 5. π-Allyl-type orbitals π1, π2, and π3 of the highlighted C-1, C-2, C-3 fragment of the anion **2a** and comparison with the orbitals π′1, π′2, and π′3 of the similarly oriented parent allyl anion. The corresponding HOMOs are π2 and π′2; the orbital contributions at the hydrogen atoms have been omitted for clarity.

Anion **2a** may therefore be regarded as an allyl anion that has been frozen on the pathway to the rotational transition state. The necessary energy is paid by forcing the allyl into the bicyclic structure, accompanied by the pyramidalization at C-1. We also expect a pyramidalization at C-3, so that **2a** is bent at the vector C-2, C-4, similarly to what has been found for the bicyclo[3.2.1]octa-2,6-dienyl anion.[21]

An obvious consequence of the charge distribution in **2a** is that its treatment with electrophiles should yield products substituted in positions 1 or 3, and this has been found for the silyl, stannyl, and plumbyl derivatives (Scheme 1 and Figure 4). The reaction at C-3 is particularly attractive as it opens a new route to bridgehead olefins. These compounds have been studied intensively[5] since the violation of Bredt's rule,[22] which states that bridgehead double bonds (in some bicyclic terpenes) should not exist. Today, several synthetic approaches to bridgehead olefins are known,[5,23] whereas the allyl route described here does not seem to have been reported yet.

Quenching of **2a** with Me_3SnCl at low temperature yielded mainly the *exo*- and *endo*-substituted bridgehead olefins **4a** and **4b**. This can be interpreted in terms of corresponding *endo*- and *exo*-face attack at C-3 of the contact ion pairs (CIPs) **2a*endo*Li** and **2a*exo*Li** shown in Scheme 3. Actually, CIPs have been established for rather similar bicyclo[3.2.1]octa-2,6-dienyl anions[21,24] in which Li^+ interacts not only with the allyl fragment but also with the nearby double bond.[25] In the case of **2a** the HOMO in Figure 5 shows that considerable negative charge is located not only at C-1 and C-3 but also at two more sites: the double bond (C-6, C-7) and the oxygen atom; hence the capability to form the different CIPs **2a*endo*Li** and **2a*exo*Li**. Subsequent reaction with Me_3SnCl may give rise to two pairs of chair and boat conformers (**4a–d** in Scheme 3).

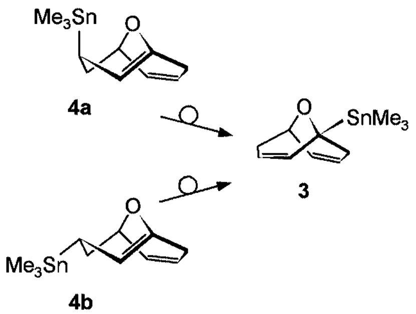


Scheme 3.

From a molecular model it is easy to see that the overlap between the π-faced orbitals at C-1 and C-2 is better for the boat conformer than for the chair. It follows that the compounds obtained here are the boat conformers. Force field calculations for structurally similar hydrocarbons have also shown the boat conformations to be more stable.[26]

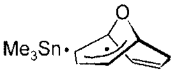
Numerous attempts to bring about reactions between the anion **2a** and transition metal derivatives were undertaken, in order to obtain π complexes such as compound **K** in Figure 2. These were all frustrated by coupling of the anion to give [**1**-H]-[**1**-H] (detected by GC/MS) and/or by yielding mixtures from which no organometallic compound could be isolated. In the light of these findings and of the fact that no anion **2b** (Scheme 2) or species of type **L** (Figure 2) could be obtained, the claims of the patent mentioned in the Introduction[6] do not appear realistic.

The time-dependent NMR measurements revealed that **4a** and **4b** are labile products that both rearrange to give the bridgehead-stannylated derivative **3** (Scheme 4). While this is an example of the well known [1,3]sigmatropic shift reactions, it is surprising from the mechanistic point of view. As can be seen from Figure 3 the consumption of **4a** and **4b** and the formation of **3** follow zero-order rate laws. The sum of the absolute rate constants $k(\mathbf{4a})$ and $k(\mathbf{4b})$ equals that of $k(\mathbf{3})$ within the experimental error, which is expected for the rearrangements in Scheme 4. For [1,3]sigmatropic rearrangements with Group 14 elements two mechanisms may be operative. In the case of carbon, diradical intermediates are involved.[27] In contrast, sigmatropic shifts of allylsilanes have been shown to be suprafacial rearrangements that occur with inversion of the silicon configuration according to experimental results,[28] while theory would favor retention of the configuration.[29] The same should be true for allylgermanes and allylstannanes.[29b] Obviously, the zero-order kinetics found here are not compatible with the sila- and stannatropic shift reactions considered so far. We believe that the activation barrier is a key to the different behavior. In compounds **4a** and **4b** the [1,3]-sigmatropic shift of the stannyl group is hampered because the π system is strongly distorted and the overlap of the allyl π MOs with the relevant MOs of the moving stannyl group is weaker (both on the inversion and the retention path[29]). In this situation the light-promoted formation of a tight radical pair of $Me_3Sn^{\cdot}$ and $\mathbf{2c}^{\cdot}$ (Figure 6) takes over and the stannyl group may settle in the more stable bridgehead position of the final product **3**. Zero-order photorearrangements are known and have recently been studied in detail in fullerene chemistry.[30] The formation of radical pairs $Me_3E^{\cdot}$ and $\mathbf{2c}^{\cdot}$ would depend on the stability of the C–E bond, which in the present case is expected to decrease in the series E = Si, Sn, and Pb. Experimentally the re-



Scheme 4.

arrangement was observed for the stannyl compounds **4a** and **4b** and the plumbyl compound **8a**, but not for the silyl compounds **6a** and **6b**, in keeping with the relative C–E bond strengths.



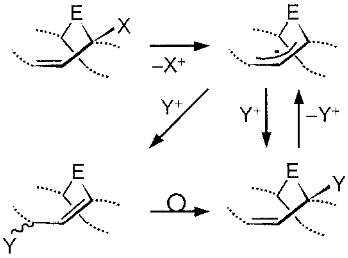
2c SnMe$_3$

Figure 6. Radical pair of $Me_3Sn^{\cdot}$ and **2c**$^{\cdot}$ formed by light induction.

Conclusion

The deprotonation of 9-oxabicyclo[3.3.1]nona-2,6-diene (**1**) with *t*BuLi in the presence of TMEDA occurs selectively in the bridgehead position and affords the bridgehead allyl anion **2a**. This is in sharp contrast with bicyclo[3.2.1]octadiene and its 9-*N*-methyl derivative mentioned in the Introduction. Treatment of **2a** with electrophiles such as Me_3SnCl provides the bridgehead-substituted derivative **3** and two bridgehead-olefin isomers **4a** and **4b**, which carry *exo* or *endo* substituents in their allylic positions. Both bridgehead olefins rearrange very slowly to revert to compound **3**. When the Me_3Sn group is replaced by Me_3Si the rearrangement cannot be observed, while it is faster for Me_3Pb. This reaction sequence is a new route both to bridgehead-substituted bicyclic compounds and to bridgehead olefins.

One can think of generalizing the approaches as illustrated in Scheme 5 by starting from a bicyclic (or polycyclic) compound containing a double bond next to the bridgehead carbon and a bridgehead proton (X = H) activated by, for example, some unit E. The stability with respect to rearrangement of the targeted bridgehead olefin derivatives should be tunable by appropriate choice of the electrophile Y used to quench the intermediate anion (i.e., by making the C–Y bond more or less labile). Y may also be chosen such that the bridgehead-substituted product is a stable derivative from which the bridgehead ally anion can conveniently be generated. In the present work this has been achieved with the stannyl derivative **3**, from which the stannyl group can be split off with alkyllithium reagents.



Scheme 5.

Experimental Section

All syntheses and manipulations were carried out with use of inert-gas (N_2) techniques and solvents that were freed from oxygen and moisture by distillation from standard reagents prior to use. Glassware was dried at 100 °C prior to use. 9-Oxabicyclo[3.3.1]nona-2,6-diene (**1**) was synthesized as described previously[8b] while all other reagents were purchased. GC/MS studies were carried out with a Hewlett–Packard 5890 Series II gas chromatograph fitted with a HP-1 column (crosslinked methylsilicone gum, 12 m × 0.2 m × 0.33 µm film, US patent 4,293,415) and coupled with a Hewlett Packard 5971 mass selective detector. The temperature program SPLTL500.M was used. The ^{1}H, ^{13}C, ^{29}Si, and $^{6/7}$Li NMR spectra were recorded with Jeol Delta 270 and 400 spectrometers while a Bruker Avance 400 spectrometer was used for measuring the ^{119}Sn NMR spectra. For referencing the signal, shifts relative to those of the deuteriated solvents (with residual protons) were calculated relative to Me_4Si [C_6H_6: $\delta(^1H) = 7.15$, $\delta(^{13}C) = 128.0$; $CHCl_3$: $\delta(^1H) = 7.24$, $\delta(^{13}C) = 77.0$]. For ^{29}Si, ^{119}Sn, and $^{6/7}$Li the external standards were Me_4Si, Me_4Sn, and a dilute solution of LiCl in water, respectively. The digital resolution was 0.1 Hz/data point for ^{1}H NMR and ≤0.3 Hz/data point in other cases. Figure 5 was obtained by Extended Hückel calculations carried out with the program package CACAO, version 4.0.[31]

Formation of 1-Trimethylstannyl-9-oxabicyclo[3.3.1]nona-2,6-diene (3) and 3-*exo*- and 3-*endo*-Trimethylstannyl-9-oxabicyclo[3.3.1]nona-1,6-diene (4a and 4b). Procedure A: A solution of *t*BuLi in hexane (8.33 mL, 1.5 M, 12.5 mmol) was diluted with hexane (50 mL) and cooled to –78 °C. Dropwise addition of TMEDA (1.87 mL, 12.5 mmol) gave a yellow solution and a white precipitate of the *t*BuLi/TMEDA complex. After addition of **1** (0.34 g, 2.8 mmol) in hexane (20 mL), and after the mixture had then been stirred while the temperature was raised from –60 °C to –30 °C over 4 h, the precipitate had disappeared and an orange solution had formed. The solution was brought to 25 °C for 5 min and cooled back to –78 °C, after which a solution of Me_3SnCl (2.5 g, 12.5 mmol) in hexane (50 mL) was added. The solution initially became colorless, and after warming to 25 °C it then became yellow and a white precipitate of LiCl formed. The mixture was quenched with water (100 mL) and the organic phase was separated and dried with $MgSO_4$. Evaporation of the solvent under vacuum gave a light yellow oil (0.29 g), which contained compounds **3**, **4a**, and **4b** in the ratio 0.39:0.25:0.36. When the starting ratios of **1**/*t*BuLi, TMEDA were 1:1 and 1:2 the corresponding ratio of the products **3**/**4a**/**4b** was 1:0:0 (for the time dependence see Figure 3). In the last two cases **3** was obtained together with side products resulting from the deprotonation of TMEDA.[32] After removal of the volatiles under vacuum for two hours, recrystallisation from hot hexane gave **3** (0.15 g) as a white powder. According to the ^{13}C NMR spectrum (Figure S1) this material contained a few impurities, so the yield is somewhat lower than the arithmetical 19 %.

Compound 3: t_R = 18.0 min; m.p. 102 °C. ^{1}H NMR (400 MHz, $C_6D_6/CDCl_3$, 3:1): δ = 5.74 (m, 1 H, 3-H), 5.72 (m, 1 H, 2-H), 5.64 (m, 1 H, 6-H), 5.59 (m, 1 H, 7-H), 4.27 (m, 1 H, 5-H), 2.55 (m, 1 H, 8-H*exo*), 2.40 (m, 1 H, 4-H*exo*), 1.77 (m, 1 H, 4-H*endo*), 1.62 (m, 1 H, 8-H*endo*), 0.09 ppm (s, 9 H, CH_3). ^{13}C NMR (100 MHz, $C_6D_6/CDCl_3$, 3:1): δ = 134.2 (C-6), 130.2 (C-2), 123.8 (C-7), 119.3 (C-3), 72.6 (C-1), 66.2 (C-5), 32.6 (C-4), 28.7 (C-8), –11.1 ppm (CH_3). ^{119}Sn NMR (149 MHz, $C_6D_6/CDCl_3$, 3:1): δ = –2.0 ppm (see Table S1 for more NMR details; Supporting Information). MS (70 eV, EI): *m*/*z*: 286 (10) $[M]^+$, 271 (100) $[M - Me]^+$, 241 (35) $[M - C_2H_5O]^+$, 165 (90) $[Me_3Sn]^+$.

Compound 4a: t_R = 17.3 min. ^{1}H NMR (400 MHz, C_6D_6): δ = 5.98 (d, 1 H, 2-H), 5.60 (m, 1 H, 7-H), 5.32 (m, 1 H, 6-H), 4.84 (m, 1 H, 5-H), 2.77 (m, 1 H, 8-H*exo*), 2.35 (m, 1 H, 8-H*endo*), 2.12 (m, 1 H, 4-H*exo*), 1.80 (m, 1 H, 3-H), 1.70 (m, 1 H, 4-H*endo*) 0.16 ppm (s, 9 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ = 154.8 (C-1), 132.9 (C-7), 130.0 (C-6), 125.8 (C-2), 81.1 (C-5), 34.1 (C-4), 33.0 (C-8), 21.3 (C-3), –8.8 ppm (CH_3). ^{119}Sn NMR (149 MHz, C_6D_6): δ = 22.0 ppm (see Table S1 for more NMR details). MS (70 eV, EI): *m*/*z*: 286 (10) $[M]^+$, 271 (45) $[M - CH_3]^+$, 241 (15) $[M - C_2H_5O]^+$, 165 (100) $[Me_3Sn]^+$.

Compound 4b: t_R = 17.3 min. ^1H NMR (400 MHz, C_6D_6): δ = 5.71 (d, 1 H, 2-H), 5.59 (m, 1 H, 7-H), 5.36 (m, 1 H, 6-H), 4.90 (m, 1 H, 5-H), 2.82 (m, 1 H, 8-H*exo*), 2.42 (m, 1 H, 8-H*endo*), 2.18 (m, 1 H, 3-H), 2.03 (m, 1 H, 4-H*exo*), 1.30 (m, 1 H, 4-H*endo*) 0.02 ppm (s, 9 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ = 161.1 (C-1), 133.2 (C-7), 129.6 (C-6), 122.6 (C-2), 83.1 (C-5), 35.5 (C-4), 33.6 (C-8), 16.4 (C-3), –11.5 ppm (CH_3). ^{119}Sn NMR (149 MHz, C_6D_6): δ = 19.0 ppm (see Table S1 for more NMR details). MS (70 eV, EI): *m*/*z*: 286 (10) $[M]^+$, 271 (45) $[M - CH_3]^+$, 241 (15) $[M - C_2H_5O]^+$, 165 (100) $[Me_3Sn]^+$.

Procedure B: A solution of *n*-BuLi in hexane (45.5 mL, 1.5 M, 68.3 mmol) was cooled to –78 °C and KO*t*Bu (7.65 g, 68.3 mmol) in hexane (200 mL) was added with stirring. Subsequently, **1** (0.3 g, 2.5 mmol) was added, whereupon the colorless mixture became yellow. Stirring and raising the temperature to 25 °C overnight gave a brown mixture, which was cooled to –78 °C before addition of Me_3SnCl (1.8 g, 9.0 mmol). The resulting colorless mixture was brought to room temperature and was quenched with water (100 mL). The organic layer was separated and dried with $MgSO_4$, and the solvent was removed under reduced pressure. Distillation of the remainder at 3 Pa and a heating-bath temperature of 100 °C gave an oil (0.8 g), which according to GC/MS analysis contained compound **3**, hexamethyl distannane, and butyltrimethylstannane in the ratio 3:1:16.

Kinetic Measurements: After workup under inert gas as described above in Procedure A, the mixture containing **3**, **4a**, and **4b** was dissolved in oxygen-free C_6D_6, transferred to a NMR tube, and sealed with a ground glass fitting and stopper. The temperature was maintained at –78 °C over crushed dry ice in a Dewar, and the NMR spectra were also run at –78 °C. In a sample that was brought to room temperature and exposed to daylight rapid rearrangement occurred. The analysis of the ^1H NMR spectra was carried out by integrating the signals of 5-H and the Me_3Sn group. Both the standard integration software and line-fitting analyses gave the same result within the error limits (Table S3, Supporting Information). The software package Origin 5.0 was used for data analysis.

Formation of 1-Trimethylsilyl-9-oxabicyclo[3.3.1]nona-2,6-diene (5) and 3-*exo*-Trimethylsilyl-9-oxabicyclo[3.3.1]nona-1,6-diene (6a): All synthetic steps were carried out as described for the stannyl derivatives under Procedure A except that $Me_3SiSO_3CF_3$ (2.41 mL, 10.84 mmol) was used for quenching the anion derived from **1**. Stripping the solvent at reduced pressure in the last step gave a colorless oil (0.12 g) containing compounds **5** and **6a** in the ratio 3:7.

Compound 5: t_R = 15.2 min. ^1H NMR (400 MHz, C_6D_6): δ = 5.74 (m, 1 H, 6-H), 5.71 (m, 1 H, 3-H), 5.65 (m, 1 H, 2-H), 5.84 (m, 1 H, 7-H), 4.36 (m, 1 H, 5-H), 2.83 (m, 1 H, 8-H*exo*), 2.45 (m, 1 H, 4-H*exo*), 2.07 (m, 1 H, 4-H*endo*), 1.71 (8-H*endo*), 0.00 ppm (s, 9 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ = 132.9 (C-2), 130.0 (C-6), 123.4 (C-7), 120.9 (C-3), 67.0 (C-1), 65.6 (C-5), 28.9 (C-4), 28.4 (C-8), –4.7 ppm (CH_3). ^{29}Si NMR (79 MHz, C_6D_6): δ = 4.8 ppm (see Table S2 for more NMR details). MS (70 eV, EI): *m*/*z*: 194 (7) $[M]^+$, 179 (100) $[M - CH_3]^+$, 121 (60) $[M - SiMe_3]^+$, 73 (90) $[Me_3Si]^+$.

Compound 6a: t_R = 15.8 min. ^1H NMR (400 MHz, C_6D_6): δ = 5.91 (d, 1 H, 2-H), 5.82 (m, 1 H, 7-H), 5.53 (m, 1 H, 6-H), 5.00 (m, 1 H, 5-H), 2.70 (m, 1 H, 4-H*exo*), 2.63 (m, 1 H, 8-H*endo*), 2.70 (4-H*exo*), 2.07 (4-H*endo*) 3-H not identified, –0.01 ppm (s, 9 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ = 155.4 (C-1), 131.4 (C-7), 130.7 (C-6), 123.2 (C-2), 81.9 (C-5), 33.6 (C-4), 30.8 (C-8), 28.4 (C-3), –3.8 ppm (CH_3). ^{29}Si NMR (79 MHz, C_6D_6): δ = 7.8 ppm (see Table S2 for more NMR details). MS (70 eV, EI): *m*/*z*: 194 (16) $[M]^+$, 179 (100) $[M - CH_3]^+$, 121 (20) $[M - SiMe_3]^+$, 73 (100) $[Me_3Si]^+$.

Formation of 1-Trimethylplumbyl-9-oxabicyclo[3.3.1]nona-2,6-diene (7) and 3-*exo*-Trimethylplumbyl-9-oxabicyclo[3.3.1]nona-1,6-diene (8a): All synthetic steps were carried out as described for the stannyl derivatives under Procedure A, except that solid Me_3PbCl (3.5 g, 12.2 mmol) was used for quenching the anion derived from **1**. Stripping the solvent at reduced pressure in the last step gave a colorless oil (1.0 g) containing compounds **7** and **8a** in 3:2 ratio.

Compound 7: ^1H NMR (400 MHz, C_6D_6): δ = 5.82 (m, 1 H, 2-H), 5.72 (m, 1 H, 3-H), 5.52 (m, 1 H, 6-H), 5.50 (m, 1 H, 7-H), 4.18 (m, 1 H, 5-H), 2.71 (m, 1 H, 8-H*exo*), 2.43 (m, 1 H, 4-H*exo*), 1.80 (m, 1 H, 4-H*endo*), 1.48 (m, 1 H, 8-H*endo*), 0.79 ppm (s, 9 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ = 132.8 (C-2), 128.8 (C-6), 124.4 (C-7), 119.2 (C-3), 67.8 (C-1), 67.5 (C-5), 34.4 (C-8), 28.3 ppm (C-4), –2.5 (CH_3) (see Table S2 for more NMR details).

Compound 8a: ^1H NMR (400 MHz, C_6D_6): δ = 6.19 [m, $^3J(^{207}Pb)$ = 51.4 Hz, 1 H, 2-H], 5.52 (m, 1 H, 7-H), 5.30 (m, 1 H, 6-H), 4.26 (br. m, 1 H, 5-H), 3.02 (m, 1 H, 8-H*exo*), 2.20 (m, 1 H, 8-H*endo*), 2.5–2.3 (4-H*exo*, severe overlap with signals of **7**), 1.6–1.3 (3-H and 4-H*endo*, severe overlap with signals of **7**), 1.19 ppm [d, $^2J(^{207}Pb, H)$ = 52.2 Hz, 9 H, CH_3]. ^{13}C NMR (100 MHz, C_6D_6): δ = 167.3 (C-1), 135.5 (C-7), 128.8 (C-6), 122.3 (C-2), 81.2 (C-5), 34.6 (C-4), 34.4 (C-8), 23.9 (C-3), –2.5 ppm (CH_3) (see Table S2 for more NMR details).

Formation of 9-Oxabicyclo[3.3.1]nona-2,6-diene-1-yllithium (2a): A NMR tube fitted with ground glass and stopper was branched to the Schlenk line, the air was replaced by dry dinitrogen, and the tube was filled with a solution of **3** (1.0 g, 3.5 mmol) dissolved in $[D_8]$THF (3 mL). While the solution was cooled to –78 °C, precooled *n*-BuLi in hexane (1.25 mL, 1.6 M, 2 mmol) was added dropwise by syringe, whereupon the solution became red. The tube was sealed and immediately inserted in the NMR probehead, which had been cooled to –50 °C. The spectra recorded at that temperature showed small signals of the starting compound and a set of signals assigned to the anion **2a**. The same experiment was carried out with *n*-Bu^{6}Li[33] for recording the ^6Li NMR spectrum.

Compound 2a: ^{13}C NMR (100 MHz, $[D_8]$THF, –50 °C): δ = 130.6 (C-6), 128.9 (C-7), 123.1 (C-2), 75.5 (C-1), 66.7 (C-5), 63.9 (C-3), 31.3 and 28.1 ppm (C-4 and C-8, tentative assignment). ^6Li NMR (58.9 MHz, $[D_8]$THF, –50 °C): δ = –0.3 ppm.

Supporting Information (see also the footnote on the first page of this article): ^{13}C NMR spectrum of compound **3**, dihedral angles of compounds **4a** and **4b**, detailed NMR spectroscopic data of compounds **3**, **4a**, **4b**, **5**, **6a**, **7**, and **8**, kinetic data for the rearrangement of compounds **4a** and **4b**.

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