Reactivity of 13,13-Dibromo-2,4,9,11-tetraoxadispiro[5.0.5.1]tridecane toward Organolithiums: Remarkable Resistance to the DMS Rearrangement†

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Reactions of dibromocyclopropane 2a, containing two spiro-fused 1,3-dioxane rings, with MeLi gave only the methylation products 8 and 9 even at elevated temperatures. In contrast, the cyclohexane analogue 2b treated with MeLi underwent a smooth rearrangement to bicyclo[1.1.0]butane 11b at −78, −10, or +35 °C. Treatment of 2a with PhLi gave the α-Ph anion 13 as the only product, which underwent smooth methylation with MeI to give 14. Under the same conditions, 2b with PhLi gave bicyclo[1.1.0]butane 11b accompanied by bromophenyl derivative 8b. Treatment of either dibromide with t-BuLi gave a mixture of products including debrominated cyclopropanes 12. Experimental results were augmented with DFT calculations for salts 23 and MP2//DFT-level calculations for carbenes 22. They demonstrated a higher stability of the dioxane R-bromo anion with respect to R-elimination by 4.8 kcal/mol and also a lower tendency of the carbene 22a to undergo rearrangement by 4.0 kcal/mol than the cyclohexane analogues. These differences have been attributed to the inductive effect of the four oxygen atoms, which results in lower LUMO energy, the higher positive charge at the carbenic center, and the overall more electrophilic character of carbene 22a as compared to the cyclohexane derivative 22b. The rearrangement of carbenes 22 to the corresponding allenes 1, the thermodynamic products, requires a higher activation energy ΔG°298 by 4.2 kcal/mol for dioxane and 6.4 kcal/mol for cyclohexane derivatives than for the formation of the bicyclo[1.1.0]butanes 11. The ΔG°298 for intramolecular insertions to the C−H bond is low and calculated as 6.0 kcal/mol for dioxane 22a and 2.0 kcal/mol for the formation of cyclohexane 22b.

Introduction

The Doering–Moore–Skattebøl (DMS) method1−3 represents a general and convenient route to substituted allenes I (Figure 1).4,5 The reaction involves a rearrangement of cyclopropylidene II, which typically is generated from the corresponding dibromocyclopropane III by lithium−halogen exchange followed by α-elimination of the bromide ion from IV.6 The rearrangement of the parent carbene has been the subject of detailed experi-

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(1) Doering, W. v. E.; LaPlume, P. M. Tetrahedron 1958, 2, 75−79.

FIGURE 1. General reaction pathways for transformation of gem-dibromocyclopropanes.

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The formation of carbene II (or a carbonoid) by α-elimination from the initial α-bromo anion IV is generally fast at temperatures above −50 °C,14 which are typical conditions for the DMS rearrangement.19 Rare cases, the α-elimination step is slow and the anion is alkylated by an alkyl halide generated in a lithium−halogen exchange reaction to form VI in quantities ranging from 2 to 13%.19,22 An electron-withdrawing heteroatom is usually present in these cases, and the alkylolation has been attributed to the stability of the bromolithium intermediate IV resulting from intramolecular coordination with oxygen12,23,24 or sulfur.25 In other cases, an alkyl halide was added to the reaction mixture at temperatures < −70 °C to avoid the DMS rearrangement and to obtain the desired alkylolation product.25,26

In the course of our work on functionalized spirocyclic systems, we focused on protected tertakis(hydroxymethyl)allene 1a and envisioned its formation by the DMS rearrangement of the corresponding dibromocyclopropane 2a (Scheme 1). This expectation was based on the reported efficient rearrangements of the cyclopropyl27 and cyclobutyl28 analogues of 2a to the corresponding allenes. Surprisingly, the precursor 2a demonstrated a significant resistance to the rearrangement, and neither desired allene 1a nor other products of rearrangement could be detected directly. For a better understanding of this result, we also investigated a similar reaction with the cyclohexane analogue 2b.

Here, we report the preparation of cyclopropanes 2a and 2b and their reactions with MeLi, PhLi, and i-BuLi. The experimental data presented in the Results were augmented with computational analysis and constitute the basis for mechanistic considerations presented in the Results.

Results

Synthesis of Dibromocyclopropanes 2. The synthesis of dibromide 2 was accomplished by dibromocarbene addition to the corresponding alkene 3 (Scheme 2). Cyclopropanation of 5,5′-bi[1,3-dioxanylidene] (3a) under PTC conditions29 overnight resulted in a mixture of starting material and dibromide 2a in a 2:3 ratio (determined by 1H NMR), and the product was isolated in about 35% yield after 3 days of stirring. In contrast, the cyclopropanation reaction of olefin 3b under identical conditions went to completion overnight, and dibromide 2b was obtained in 55% yield. In an attempt to improve the yield of 2a, PhHgCBr3 was used as the source of dibromocarbene recommended for weakly nucleophilic olefins.30 Thus, a reaction of 3a with 1.5 equiv of PhHgCBr3 proceeded to about 50% conversion, and cyclopropane 2a was isolated in 28% yield.

The preparation of olefin 3a was reported in the literature as a component of a mixture or a sole product of a reaction between 5-bromo-5-nitro-[1,3]dioxane (4) and EtSNa31 or the lithium salt of 5-nitro-[1,3]dioxane32 (5) in DMSO (Scheme 3). The reported 80% yield of 3a could not be reproduced despite our efforts. Numerous reactions closely following the literature procedure31 and using either carefully dried reagents under strictly anaerobic atmosphere or just reagent grade DMSO gave the same and lower yields of 3a.


Scheme 1

\[
\begin{align*}
\text{SCHEME 1} \\
\text{Br} & \quad \text{Br} \\
\text{R} & \quad \text{R} \\
\text{II} & \quad \text{II} \\
\text{V} & \quad \text{V} \\
\end{align*}
\]

Scheme 2

\[
\begin{align*}
\text{SCHEME 2} \\
\text{Br} & \quad \text{Br} \\
\text{R} & \quad \text{R} \\
\text{II} & \quad \text{II} \\
\text{V} & \quad \text{V} \\
\end{align*}
\]
consistent results of 20%–30% yield. We noticed, however, low mass recovery from the reaction mixture, which was presumably due to partial water solubility of olefin 3a or products of dioxane ring opening. Most organic material was recovered from the aqueous workup in the first three extractions with benzene, and additional extractions or even continuous extraction gave only traces of organic products. Reducing the volume of originally used DMSO by substituting approximately 50% of it with benzene did not affect the yield of 3a.

While optimizing the single-step preparation of 3a, we were simultaneously searching for an alternative method for its preparation. In particular, we focused on reduction of vicinal dinitroalkanes with “NiB”, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields. In particular, we focused on reduction of vicinal dinitroalkanes, which was reported to give good preparatory yields.

The dioxane derivative 2a showed limited solubility in ether at the temperatures below 0 °C, and most of its reactions were run at −10 °C at low concentrations (~10 mM). For instance, 2a partially precipitated from 8 mM solutions at −78 °C. Experiments with both dibromides demonstrated that the lithium-halogen exchange reactions with 1.1 equiv of MeLi were inefficient for the 10 mM solutions of 2, and most (~90%) of the starting material was recovered contaminated with <5% of mono bromide 7.

Reactions of dioxane derivative 2a with 2.2 equiv of MeLi at −10 °C gave the monobromo derivative 7a as the main product accompanied by small amounts of the bromomethyl product 8a (R = Me), both isolated in a combined yield of ~95% (entry 1). The same reaction run in hot ether (entry 2) did not give the protonated product 7a, and instead the dimethyl derivative 9a and bromo methyl 8a (R = Me) were formed in equal amounts as the sole products. This suggests that the α-bromocarbaborane derived from 2a in part reacts slowly with MeBr at ambient temperature and, in part, is protonated during workup. Some support for this scenario was provided by the next experiment (entry 3) in which 2a was treated first with 2.2 equiv of MeLi, and after 5 min excess MeLi was added at −10 °C. No protonation product 7a was detected, and the bromo methyl 8a (R = Me) and dimethyl 9a were the main products formed in an 3:2 ratio. The reaction mixture also contained about 20% of unreacted dibromide 2a, which suggests that 5 min is insufficient time for complete lithium–halogen exchange and that a reaction between MeLi and Me is faster than lithiation of 2a. With higher MeLi to 2a ratios, the dimethylated product 9a dominated and traces of another product, presumably 10a (R = Me), were occasionally detected.

Attempts at separation of the complex mixtures into individual components by either chromatographic methods or recrystallization were largely unsuccessful. Instead, reaction products were identified by NMR and MS techniques, and the formation of 1a or possible bicyclo[1.1.0]butane 11a in quantities >1% can be excluded. NMR analysis showed that all products have high molecular symmetry, and the olefinic 1H or 13C signals were completely absent in either crude or chromatographically isolated mixtures of products.

Initial experiments with MeLi indicated that methylation with MeBr of the transient α-bromocarbaborane derived from 2a is faster than the loss of bromide ion and rearrangement. To avoid the presence of the strongly electrophilic MeBr in the reaction mixture, we investigated reactions of 2a with PhLi and t-BuLi. The first reagent generates the nonelectrophilic PhBr in the lithium–halogen exchange with 2a, while t-BuLi gives t-BuBr, which is quickly destroyed by excess t-BuLi.

Reactions of 2a with PhLi gave an unexpected result. At a low PhLi:2a ratio (entry 4), half of the starting dibromide reacted giving equal amounts of the protonated anion 7a and the product of phenylation (!) 10a (R = Ph), according to GC/MS analysis. When 5 equiv of PhLi was used (entry 5), the sole product was 10a (R = Ph) isolated in 63% yield. GC/MS analysis demonstrated that the reaction was complete after 10 min at −10 °C, and no intermediates were observed. Addition of PhLi to 2a in boiling ether (35 °C) had little effect on the reaction outcome, and 10a (R = Ph) was formed cleanly as the
TABLE 1. Product Distribution in Reactions of Dibromocyclopropanes 2 with RLi

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>R-Li (equiv)</th>
<th>T (°C)</th>
<th>2</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a</td>
<td>Me</td>
<td>-10 → rt</td>
<td>85a</td>
<td>10a</td>
<td>45a</td>
<td>45a</td>
<td>20b</td>
<td>30b</td>
<td>20b</td>
</tr>
<tr>
<td>2</td>
<td>X = O</td>
<td>Me</td>
<td>35</td>
<td>20c</td>
<td>20c</td>
<td>20c</td>
<td>20c</td>
<td>20c</td>
<td>20c</td>
<td>20c</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>Me + MeI</td>
<td>-10 → rt</td>
<td>20a</td>
<td>20a</td>
<td>20a</td>
<td>20a</td>
<td>20a</td>
<td>20a</td>
<td>20a</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>2.5</td>
<td>-10 → rt</td>
<td>55b</td>
<td>20b</td>
<td>30b</td>
<td>30b</td>
<td>30b</td>
<td>30b</td>
<td>30b</td>
</tr>
<tr>
<td>5</td>
<td>Ph</td>
<td>5</td>
<td>-10 → rt or 36</td>
<td>50b</td>
<td>50b</td>
<td>50b</td>
<td>50b</td>
<td>50b</td>
<td>50b</td>
<td>50b</td>
</tr>
<tr>
<td>6</td>
<td>tert-But</td>
<td>1.1</td>
<td>-80 → -10</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
</tr>
<tr>
<td>7</td>
<td>tert-But</td>
<td>5</td>
<td>-10</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
<td>70b</td>
</tr>
<tr>
<td>8</td>
<td>2b</td>
<td>Me</td>
<td>5.3</td>
<td>60b</td>
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<td>X = CH2</td>
<td>Ph</td>
<td>-10 → rt</td>
<td>60b</td>
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<tr>
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<td>10b</td>
<td>10b</td>
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</tr>
<tr>
<td>11</td>
<td>tert-But</td>
<td>2.5</td>
<td>-80 → -10</td>
<td>30c</td>
<td>30c</td>
<td>30c</td>
<td>30c</td>
<td>30c</td>
<td>30c</td>
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</tr>
<tr>
<td>12</td>
<td>tert-But</td>
<td>2.5</td>
<td>-80</td>
<td>50c</td>
<td>50c</td>
<td>50c</td>
<td>50c</td>
<td>50c</td>
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<td>50c</td>
</tr>
<tr>
<td>13</td>
<td>tert-But</td>
<td>5</td>
<td>-80 → -10</td>
<td>70c</td>
<td>70c</td>
<td>70c</td>
<td>70c</td>
<td>70c</td>
<td>70c</td>
<td>70c</td>
</tr>
</tbody>
</table>

a From NMR ratio of products in isolated mixture. b From GC/MS ratio of products in the crude mixture. c Isolated yield. d Diene 19 was isolated in 37% yield and 90% purity. e No 7a was observed at 3× higher concentration of 2b in ether.

SCHEME 4

sole product. To demonstrate that α-phenylcarbanion 13 is involved in the formation of 10a (R = Ph), Mel was added to the reaction mixture before quenching with water. In this case, the methyl derivative 14 was formed as the only product, which was isolated in 89% yield (Scheme 4).

Reactions of 2a with tert-ButLi were generally less clean than those with MeLi or PhLi. Thus, a reaction of 2a with 1.1 equiv of tert-ButLi gave a mixture consisting mostly of the starting material and monobromide 7a in a 1:1 ratio by GC/MS. When 2a was treated with 5 equiv of tert-ButLi at -10 °C, all starting dibromide 2a was consumed, and the isolated reaction mixture (>70% of the theoretical amount) consisted of three main products (entry 7). Two of them were identified as tert-butyl derivative 10a (R = tert-But) and the debrominated product 12a in a ratio of about 2:5 by GC/MS or 1:4 by NMR. The mixture was partially separated giving the first fraction containing mainly 10a (R = tert-But), the second fraction containing mainly 12a, and the third fraction as a mixture of 12a and the unknown component(s) in a 2:1 ratio. Analysis of the NMR spectra of the last fraction revealed that the unknown component(s) had olefinic signals in the range of 111–114 and about 142 ppm, in addition to the aliphatic signals in the high field. The olefinic byproduct could be formed by attack of tert-ButLi on the acetal group of the dioxane ring. However, their formation by a reaction of tert-ButLi with the transient bicyclo[1.1.0]butane 11a cannot be excluded. Monobromide 8a (R = tert-But) was never observed in these reactions by GC/MS or by NMR methods.

When the same reaction was conducted at -80 °C instead of -10 °C using a total of 6 equiv of tert-ButLi, GC/MS and NMR analysis showed significantly less of the unidentified byproduct. Both 10a and 12a were isolated chromatographically in 6% and 27% yields, respectively, and independently characterized.

In all reactions of 2a with RLi, mass recovery of organic products was high, often close to the theoretical amount. No cyclopropylidene rearrangement products, neither allene 1a nor bicyclo[1.1.0]butane 11a, were observed directly among the reaction products. Only in reactions with tert-ButLi at -10 °C could 2a form 11a as a transient species.

In contrast to the reactivity of 2a, treatment of the cyclohexane analogue 2b with organolithium reagents gave bicyclo[1.1.0]butane 11b as either the exclusive (reactions with Mel, entry 8) or a significant (reactions with PhLi and tert-ButLi) product. Also, many of the products observed in reactions of dioxane 2a with organolithium reagents were not detected in the analogous reactions of 2b. The 13C NMR spectrum of crude freshly prepared 11b showed no molecular symmetry and no olefinic signals. During chromatographic separation, attempted distillation, or even storage at ambient temperature for over 1 day, 11b decomposed to form two isomeric olefinic products in a ratio of about 4:1 (NMR). This ratio changed to 9:1 (NMR) upon further chromatographic purification (SiO2, hexanes). On the basis of NMR and MS analysis, the two olefins were assigned structures 15 (major) and 16 (minor), respectively (Scheme 5). Further support for the assignment was provided by a close match of the NMR spectra with those reported for the two olefins prepared by other routes.40,41

The proposed mechanism for proton-catalyzed ring opening in bicyclo[1.1.0]butane 11b and the formation of the dienes

shown in Scheme 5 is consistent with literature data for other bicyclo[1.1.0]butanes and the pathways for their ring-opening processes. Support for the proposed mechanism is also provided by the occasional isolation of cyclohexanol 17 apparently formed by the hydration of the intermediate cation 18 (Scheme 5).

The reaction of 2b with PhLi at −10 °C (Table 1, entry 9) gave the expected bicyclo[1.1.0]butane 11b and, surprisingly, phenyl derivative 8b (R = Ph) in approximately 2:3 ratio (NMR). The ratio was temperature sensitive, and at higher temperatures more bicyclo[1.1.0]butane 11b was formed. Thus, the same reaction run at 35 °C (Table 1, entry 10) was completed after 10 min, and the 11b/8b ratio was ~8:1. Upon attempted chromatographic separation of the crude reaction mixture, the bromide completely rearranged to diene 19, which was isolated in 37% yield. The observed facile ionization of 8b (R = Ph) and the formation of diene 19 is consistent with a recent report of rearrangement of 1-bromo-2,2,3,3-tetramethyl-1-phenylcyclopropane in warm methanol. An independent experiment demonstrated that bicyclo[1.1.0]butane 11b is stable to PhLi at ambient temperatures for at least several hours. The ionization of the formally cumylic bromide 8b (R = Ph) permits a 2π electrocyclic cyclopropane ring opening to form the allyl cation 20, which upon the subsequent elimination of a proton gives the diene 19 (Scheme 6).

Reactions of 2b with t-BuLi gave bicyclo[1.1.0]butane 11b and smaller amounts of debrominated product 12b. In reactions with low t-BuLi/2b ratios, monobromide 7b was also observed in addition to 11b and 12b. The proportions of the products depended on the amounts of the organolithium and reaction temperature, and also varied somewhat from run to run. In one

SCHEME 5

SCHEME 6

set of experiments with 2.5 equiv of t-BuLi, less bicyclo[1.1.0]butane 11b was produced and lower 11b/12b ratio was observed at −80 °C (entry 11) than when the reaction was run at −10 °C (entry 12). When 5 equiv of t-BuLi was used (Table 1, entry 13), monobromide 7b was completely absent, and the mixture contained bicyclo[1.1.0]butane 11b and debrominated product 12b as the sole products in about 4:1 ratio. The ratio was practically the same whether the reaction mixture was quenched with cold EtOH at −78 °C or poured into EtOH or water at ambient temperature.

Finally, a competition experiment was conducted in which a 1:1 equimolar mixture of dibromocyclopropanes 2a and 2b was reacted with 1.1 equiv of MeLi. GC/MS analysis showed that dioxane dibromide 2a was completely consumed forming the monobromide 7a, while only about 10% of the cyclohexyl dibromide 2b was converted to 11b as evident from GC/MS and 1H NMR of the crude reaction mixture.

Theoretical Analysis. To better understand the experimental results and to support structural assignment of the observed products, we investigated the formation and rearrangement of several relevant carbones, and calculated the NMR chemical shifts for selected products at the B3LYP level of theory.

Conformational Analysis. The dioxane and cyclohexane dirsepo derivatives can exist in three main conformational forms shown in Figure 2. Calculations at the B3LYP/6-31+G(d,p) level for the dioxane derivatives revealed that thermodynamic stability of the conformers follows the order B > A > C, which parallels the trend in their net molecular dipole moments. Conformers of type A are less stable than those of type B by about 1.0−1.5 kcal/mol, while conformers of type C are still less stable by an additional ~1 kcal/mol.

Conformers A and B of the cyclohexane derivatives appear to have similar thermodynamic stability with a conformer of type A being slightly favored, e.g., by 0.2 kcal/mol for 12b. On the basis of these results, calculations of carbene formation and subsequent rearrangement to either 1 or 11 typically involved conformers of type B for dioxane derivatives and conformers of type A for the cyclohexane analogues. NMR calculations (vide infra) use the relative stability of the conformers to calculate weighted average chemical shifts of selected products. Detailed numerical information is given in the Supporting Information.

Carbene Formation. Gas-phase calculations for anions 21 show that the loss of Br− ion and the formation of the corresponding carbene 22 is endothermic. For the parent cyclopentadiene 22c, the endotherm is about 20 kcal/mol (Table 2), and this energy increases by about 3.5 kcal/mol per added cyclohexane unit to 26.8 kcal/mol for 22b.56 In contrast, α-elimination from anion 21d containing one dioxane ring is more endothermic by about 12 kcal/mol relative to the parent 21c and by nearly 20 kcal/mol from anion 21a containing two

TABLE 2. Calculated Energies for the Formation of Carbenes in the Gas Phase.

<table>
<thead>
<tr>
<th>Reaction 1</th>
<th>Reaction 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>R R R' 1</td>
<td>ΔH kcal/mol</td>
</tr>
<tr>
<td>a</td>
<td>39.3</td>
</tr>
<tr>
<td>b</td>
<td>26.8</td>
</tr>
<tr>
<td>c H H H H</td>
<td>19.8</td>
</tr>
<tr>
<td>D O O H H</td>
<td>31.7</td>
</tr>
<tr>
<td>E O O O O</td>
<td>23.3</td>
</tr>
</tbody>
</table>

a B3LYP/6-31+G(d,p) level of theory. b The Li⁺ interacts with the ring’s oxygen atoms. c The Li⁺ does not interact with the ring’s oxygen atoms.

SCHEME 7

Addition of dioxane rings to 23c has a more pronounced effect on the enthalpy of elimination. Thus, the first dioxane ring increases the enthalpy of complex elimination by nearly 5 kcal/mol in 23d. Intramolecular coordination of the Li⁺ ion by the ring’s oxygen atoms in 23d moderately stabilizes the salt, and consequently, the enthalpy of elimination increases by 0.7 kcal/mol. Addition of the second dioxane ring increases this enthalpy by 5 kcal/mol in 23a in which the Li⁺ ion is internally coordinated. Free energy change for these reactions is graphically shown in Figure 3. Interestingly, coordination of the Li⁺ ion to dioxane’s oxygen atoms decreases the endergonicity of the complex elimination in spite of increased endotherm of the reaction. This is due to lowering of entropy of 23b by 7 cal/mol·K upon intramolecular coordination of the Li⁺ ion.

The results demonstrate that the dioxane salt 23a is more stable toward elimination and carbene formation than the cyclohexane analogue 23b by about 5 kcal/mol.

Stabilization of carbenes by coordination to a molecule of ether appears to be modestly exothermic for cyclopropyldiene 22c forming 24c, but due to the significant entropy decrease (−38 cal/mol·K) the process is still endergonic at this level of theory (Scheme 7). This small energy gain in stabilization of 22c is insufficient to offset the 15.6 kcal/mol endotherm of the elimination of the LiBr complex from 23c, and the whole process is significantly endergonic due to the net negative entropy change. Calculations at the MP2/6-31+G(d,p)//B3LYP/6-31+G(d,p) level with the DFT thermodynamic corrections lower this energy by 7.7 kcal/mol, and the resulting free energy change for the formation of 24c from carbene 22c is nearly zero. This suggests that complex 24c is in equilibrium with carbene 22c, and the calculations for the free carbene in gas phase provide a reasonable approximation of the solution reactivity.

The optimized geometry of the parent salt 23c converged at the C₃ point group symmetry (Figure 4). The Me₂O, Li, and Br lie in the symmetry plane, which is orthogonal to the cyclopropane ring. The Me₂O and cyclopropane fragments are connected by the Li⁺ ion, which is also coordinated to the Br atom. The resulting C—Li···OMe₂ and C—Li···Br angles are 171° and 130°, respectively. The Li···OMe₂ and Li—C distances (1.89 Å and 1.96 Å, respectively) found in the parent salt 23c are approximately constant in the series of salts 23, while the Br—C and Br···Li distances vary in response to the structural changes.

The C—Br distance, d_{C—Br}, in the parent salt 23c (2.22 Å) is practically unchanged, and the Br···Li separation (2.44 Å) is shortened by 0.01 Å upon appending the cyclohexane rings. In contrast, the d_{C—Br} decreases by 0.06 Å with simultaneous increase of the Br···Li distance by 0.03 Å upon appending the first dioxane ring in 23d. Moving the lithium atom toward the dioxane oxygen atoms in 23d trades the coordination of the cation by the bromine atom (d_{Li—Br} = 2.94 Å) for the ring oxygen atom (d_{Li—O} = 2.14 Å) and leads to the contraction of

(47) A reliable theoretical description of the stability of a dative bond such as that in 24c is provided by the MP2 method.
the C–Br distance by 0.08 Å. In the bisdioxane salt 23a in which the Li+ ion is also internally coordinated, the C–Br distance is further reduced by 0.01 Å and the Li–C separation is slightly enlarged to 2.00 Å. Overall, the C–Br distance in 23a is shorter by 0.15 Å than that in cyclohexane analogue 23b.

A similar trend in the shortening of the C–Br distance, d_{C-Br}, upon addition of dioxane rings in salts 23 is also found for the bromo anions 21d and 21a. Thus, in 21d the d_{C-Br} decreases by 0.04 Å relative to the parent 21c and by an additional 0.03 Å (to 2.09 Å) in 21a. For the cyclohexane analogues 21e and 21b the d_{C-Br} decreases by about 0.01 Å per added ring.

The observed trends in the Br–C bond lengths in both series of compounds 21 and 23 parallel the trends in the energetics of the carbene formation from the two substrates.

**Carbene Electronic Properties.** Analysis of NBO wave functions for the series of carbones 22 shows that the HOMO involves an sp^0.5 hybridized orbital of the carbenic atom, while the LUMO is essentially a pure p orbital orthogonal to the cyclopropylidene ring (Figure 5). The energies of the LUMO and HOMO orbitals are gradually increasing upon substitution with the cyclohexane rings. In contrast, the LUMO, which is responsible for the electrophilic properties, gradually decreases in the series of dioxane analogues, while the HOMO remains practically unchanged (Figure 6). Thus, addition of the cyclohexane rings increases nucleophilic properties of the carbene, while dioxane rings enhance its electrophilic properties, which is consistent with the general trend in philicity of carbenes and their reactivity with alkenes.48 This conclusion for carbones 22 is further supported by an analysis of the charge density, which demonstrated that the carbene center retains approximately the same charge for the cyclohexane derivatives, 22b and 22c, and the parent 22c (+0.19), while in the dioxane analogues 22d and 22a the charge is higher (+0.21). Interestingly, the orientation of the cyclopropylidene with respect to the dioxane ring has a significant effect on the properties of the carbene. For the equatorial orientation of the carbenic center in 22d-eq, the LUMO is lower by 0.19 eV than in the axial conformer 22-ax, while the enthalpy difference between the two conformers is only 0.15 kcal/mol. This suggests that stereoelectronic interactions (such as those in the anomic or gauche effects) exist between the oxygen atoms and the carbenic center.

**Carbene Rearrangement.** Investigation of the rearrangement of two singlet carbones 22a and 22b revealed that the formation of either the corresponding allenes 1 or bicyclo[1.1.0]butanes 11 is a highly exothermic process characterized by a relatively

---

The calculated \( \Delta G^{298} \) values are greater for the dioxane carbene \( 22a \) than for the analogous transformations of the cyclohexane analog \( 22b \). A comparison of the calculated activation energies with those for two model carbenes, the parent cyclopropylidene (\( 22c \)) and tetramethylcyclopropylidene (\( 22f \)), is particularly informative (Table 3). Thus, activation energies for the rearrangement of the cyclohexane and tetramethyl carbenes, \( 22b \) and \( 22f \), to the corresponding allenes are similar and nearly 5 kcal/mol higher than that obtained for the transformation of the parent cyclopropylidene (\( 22c \)) to allene \( 1c \). This significant increase of \( \Delta G^{298} \) for \( 22b \) and \( 22f \) and also \( 22a \) (about 7 kcal/mol) is contrary to expectations based on results for cis-2,3-dimethylcyclopropylidene and is presumably related to steric interaction of the four substituents in the ring opening TS.

Further inspection of the computational results for both carbenes \( 22a \) and \( 22b \) shows that the formation of bicyclo[1.1.0]-butanes \( 11 \) is significantly easier (kinetic products) than the rearrangement to the corresponding allenes \( 1 \), which are the thermodynamic products. The calculated activation enthalpy for the \( \text{C}-\text{H} \) insertion process in all three carbenes \( 22 \) is in the range of 1–4.6 kcal/mol, which is consistent with activation energies calculated for the insertion of methylene to methane and ethane at a similar level of theory. The difference between the free energies of activation \( \Delta G^\text{a} \) for the two competing rearrangements of carbenes \( 22 \) is >4 kcal/mol, which suggests that bicyclo[1.1.0]-butanes \( 11 \) are practically the only expected products. The calculated low activation energies for the \( \text{C}-\text{H} \) insertion process (\(<6.0 \text{ kcal/mol}\) further suggests that the rearrangement of \( 22b \) to \( 11b \) should be observed even at low temperatures. The fact that only rearrangements of \( 22b \) to \( 11b \) and \( 22f \) to \( 11f \) are observed experimentally indicates the difficulties with the formation of the dioxane carbene \( 22a \), which is consistent with the computational results for anions \( 21 \) and \( 23 \).

Analysis of the transition-state geometry for the allene rearrangement revealed that the tetramethyl and cyclohexane structures \( 1f-\text{TS} \) and \( 1b-\text{TS} \) have the \( C_3 \) symmetry and the shortest in the series \( C(2)\cdots C(3) \) distances of 1.778 and 1.834 Å (Figure 4), respectively. In contrast, transition states \( 1c-\text{TS} \) and \( 1a-\text{TS} \) are asymmetric, and the degree of deviation from the \( C_3 \) geometry follows the trend in the \( C(2)\cdots C(3) \) separation. Thus, for \( 1a-\text{TS} \) with the \( C(2)\cdots C(3) \) distance of 1.848 Å the parameters \( \delta_1 \) and \( \delta_2 \) are small (6° and 12°) and they increase to 12° and 17° for \( 1c-\text{TS} \) for which the \( C(2)\cdots C(3) \) is the longest (1.995 Å). This is consistent with the extensive analysis

### Table 3. Calculated Thermodynamic Parameters for Rearrangement of Cyclopropylidene

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition State</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>symmetry ( \Delta H_{298}^S ) kcal/mol</td>
<td>( \Delta G_{298}^S ) kcal/mol</td>
</tr>
<tr>
<td>la</td>
<td>C(_1)</td>
<td>11.0</td>
</tr>
<tr>
<td>11a</td>
<td>C(_1)</td>
<td>4.6</td>
</tr>
<tr>
<td>lb</td>
<td>C(_2)</td>
<td>9.2</td>
</tr>
<tr>
<td>11b</td>
<td>C(_1)</td>
<td>1.0</td>
</tr>
<tr>
<td>1c</td>
<td>C(_1)</td>
<td>3.9(^a)</td>
</tr>
<tr>
<td>1f MeMe</td>
<td>C(_3)</td>
<td>8.9</td>
</tr>
<tr>
<td>11f MeMe</td>
<td>C(_1)</td>
<td>1.8</td>
</tr>
</tbody>
</table>

\( ^a \) MP2/6–31+G(d,p)//B3LYP/6–31+G(d,p) level of theory with DFT thermodynamic corrections. Symmetry of the starting carbenes: \( 22a-C_3 \), \( 22b-C_2 \), \( 22c-C_2v \), \( 22f-C_2\). This value is consistent with that obtained with the CCSD/CASSCF (3.6 kcal/mol) or CCSD/CISD (4.2 kcal/mol) methods (ref9) and is lower by 1.3 kcal/mol than that calculated at the DFT/DFT level of theory.

products that do not contain bromine (52). Further support for the structural assignment to the observed

\[
2\text{CH}_3\text{X}+2\text{CH}_2\text{X}+3\text{CH}_2\text{X}_2\text{CH}_3+2(\text{CH}_3)\text{CH}+2(\text{CH}_3)\text{C}
\]

\[
11\text{a}, \text{x} = \text{O}, \text{SE} = 58 \text{ kcal/mol}
\]

\[
11\text{b}, \text{x} = \text{CH}_2, \text{SE} = 64 \text{ kcal/mol}
\]

\[
\text{theory} \quad \text{SE} = 64 \text{ kcal/mol}
\]

\[
\text{experiment} \quad \text{SE} = 66 \text{ kcal/mol}
\]

**FIGURE 7.** Strain energy (SE) calculated from SCF energies at the B3LYP/6-31+G(d,p) level of theory using a homodesmotic reaction. Experimental SE for the parent bicyclo[1.1.0]butane taken from ref 52 for the parent cyclopropyldiene,\(^9\) according to which the ring opening process initially follows the disrotatory symmetric motion of the two CR\(_2\) groups characteristic for a 2e concerted process. In the vicinity of the TS one of the CR\(_2\) groups begin to rotate faster destroying the C\(_1\) symmetry. For the parent cyclopropyldiene 1c, this asymmetric motion begins at about 1.85 Å,\(^9\) which is consistent with the observed symmetric TS for cyclohexane 1b-TS (1.834 Å) and asymmetric TS for
dioxane 1a-TS (1.848 Å).

The intramolecular insertion of carbene into the C–H bond and the formation of the bicyclo[1.1.0]butane derivative 11 is a concerted process\(^49\) in which the vacant p orbital interacts with the C–H bond, while the hydrogen moves to the carbenic sp\(^3\), hybridized orbital. In the transition state for rearrangement of both 22a and 22b, the C–H is elongated by about 0.15 Å and the H···C(1) distance is about 1.5 Å. The C(1)···C distance is about 1.95 Å. The C–C bond formation and the hydrogen transfer are both more advanced in the cyclohexane 1b-TS by about 0.04 Å than in the dioxane 1a-TS.

**Strain Energy (SE).** Strain energies (SEs) for the two bicyclo[1.1.0]butanes, the expected 11a and the observed 11b, were obtained using a homodesmotic reaction\(^51\) and compared to that of the parent bicyclo[1.1.0]butane. The results shown in Figure 7 demonstrate that the SE for the cyclohexane derivative 11b is identical to that obtained for the parent, which in turn is close to that obtained from experimental heats of formation.\(^52\) The SE for the dioxane derivative 11a is lower by 6 kcal/mol than that of 11b. However, considering that analogous calculations for [1,3]dioxane give SE of −2 kcal/mol, the overall strain of 11a is similar to that of the cyclohexane derivative 11b.

Analysis of the molecular geometry for the three bicyclo[1.1.0]butanes showed no unusual differences, except for the length of central C–C bond. It is longer for 11a (1.509 Å) than for cyclohexane 11b (1.500 Å) and for the parent (1.494 Å).

**NMR Structural Assignment.** Among 10 primary and 5 secondary products of reactions of 2a and 2b with RLi, 5 were isolated in their pure forms. The remaining compounds were secondary products of reactions of 2a, 2b, or RLi. The reaction pathways observed for both substrates are summarized in Scheme 8.

The cyclohexane derivative 2b smoothly forms the lithium salt 23b upon treatment with MeLi, which subsequently undergoes elimination of LiBr. The resulting carbene 22b (or carbenoid) rearranges to bicyclo[1.1.0]butane 11b in a nearly quantitative yield. The step of LiBr elimination is fast even at low temperature, and no methylation products are observed. This indicates that reaction rates for elimination are greater than alkylolation (k\(_{5b} \gg k_{5b}\) and k\(_{2b} \gg k_{3b}\) in Scheme 8) and also that the rate for C–H insertion is greater than rearrangement to allene 11b (k\(_{4b} \gg k_{3b}\)) in Scheme 8). The latter is consistent with the computed lower free energy of activation for the formation of 11b than for the formation of allene 1b by 6.4 kcal/mol (Table 3) and with reports of the preferential formation of bicyclo[1.1.0]butanes by some other tetrasubstituted gem-dibromocyclopropanes.\(^{10,11,14}\)

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(50) Parameters \(\delta\) are 0° for \(C_\alpha\)-symmetric geometry and 90° for \(D_2\) allene.

For the definition, see ref 9.


Reactivity of 13,13-Dibromo-2,4,9,11-tetraoxadispiro[5.0.5.1]tridecane

In contrast, salt 23a derived from dioxane derivative 2a and MeLi undergoes efficient methylation with MeBr to yield 8a. This indicates that \( k_{2a} \ll k_{3a} \) for the dioxane derivative and also that the activation energy for LiBr elimination is significantly higher than that for methylation of the anion. Assuming that the rates of methylation of either anion 23a or 23b are similar \( (k_{3a} \sim k_{3b}) \), the rate of LiBr elimination from the former is significantly lower than that from the cyclohexyl derivative 23b \( (k_{2a} \ll k_{2b}) \). This is consistent with the computed higher endergonicity for the formation of carbene 22a by nearly 5 kcal/mol than the formation of 22b from the respective salts 23 (Table 2). In the presence of excess MeLi, bromide 8a undergoes Li—halogen exchange, and the resulting anion 10a\^\* is methylated again giving the dimethyl derivative 9a.

Reactions of dibromides 2a and 2b with PhLi gave surprising results highlighting again the differences in the reactivity of the two compounds. Thus, reactions of the cyclohexane dibromide 2b with PhLi gave the expected bicyclo[1.1.0]butane derivative 11b, but, surprisingly also the bromide 8b \( (R = \text{Ph}) \) was formed as the only byproduct. The formation of 8b can be explained as a coupling of a caged radical pair\(^{57} \) that is formed during the metal-halogen exchange (MHE) process in accordance with a general mechanism\(^{58} \) involving a single electron transfer (SET) process (Scheme 9). The proposed mechanism for the formation of 8b is consistent with the observations that (i) the amount of 8b appears to be greater at lower temperatures and at lower concentrations and (ii) no other byproduct are observed in significant amounts.

A reaction of the dioxane dibromide 2a with PhLi proceeds differently than that of the cyclohexane analog. In this case, the initially formed bromoanion 23a apparently undergoes a facile nucleophilic substitution with excess PhLi to give salt 10a—Li⁺, which is either protonated to give 10a or methylated with MeL to give 14 as the exclusive products. This indicates again that the rate for LiBr elimination from 23a to form carbene 22a is significantly lower than those for the competing processes, including a reaction of the anion with PhLi \( (k_{2a} \gg k_{2b}) \) and also bicyclopropylidenes\(^{26,69} \). The computational results show however, that there is no significant loosening of the C—Br bond in the dioxane derivative 23a as postulated in MAI and experimentally observed for some carbeneoids\(^{18} \). Instead, the C—Br bond in 23a is shorter by 0.15 Å than that in the cyclohexane analogue 23b. Moreover, the Li⁺ ion is coordinated to the ring’s oxygen atoms, which opens the carbon center for nucleophilic attack. Therefore, a more appropriate description for the process observed in 2a should be coordination-assisted nucleophilic substitution (CANS) as shown in Figure 9. Interestingly, this mechanism does not seem to operate for reactions of 2a with MeLi, presumably due to the presence of MeBr. The observation of bromide 8a \( (R = \text{Me}) \) in reactions with MeLi (Table 1) as the primary product indicates that in this case \( k_{2a} > k_{2b} \). The formation of methylation byproduct (analogues of 8—10) and also bicyclopropylienes (products of self-condensation) in reactions of some dibromocy-
clopropanes with MeLi has been reported in the literature, but always as minor components of mixtures of products.

Results for reactions of dibromides 2a and 2b with t-BuLi are consistent with those obtained with MeLi and PhLi, although they are complicated by the presence of t-BuBr formed in the metal—halogen exchange process. In the reactions of dibromide 2b with t-BuLi, the bicyclo[1.1.0]butane 11b is still the dominant product, but is accompanied by debrominated product 12b formed regardless of the reaction and quenching process temperatures. The formation of 12b can be rationalized as a competition between the α-bromo anion 23b and t-BuLi for the proton from t-BuBr (Scheme 10) on one hand, and Br− elimination and the formation of carbene (carbenoid) 22b on the other. Since the lithium—halogen exchange is a fast process, the t-BuLi that is being added dropwise to 2b is rapidly consumed leaving anion 23b and t-BuBr. Thus, at the beginning of t-BuLi addition the concentration of anion 23b is greater than that of t-BuLi, and 23b may effectively compete for the proton from t-BuBr. At low temperature, the elimination of Br− and the formation of carbene 22b is slow, and less bicyclo[1.1.0]butane 11b is formed in favor of 7b (Table 1, entry 12). At higher temperatures (−10 °C), the formation of carbene (carbenoid) and its subsequent rearrangement to bicyclo[1.1.0]butane 11b is the dominant process, and less monobromide 7b is generated (Table 1, entry 11). With the low t-BuLi/2b ratio, the excess t-BuLi is never achieved and monobromide 7b is formed in significant quantities. For the high t-BuLi/2b ratio, the generated monobromide 7b is lithiated with excess t-BuLi that is built up at the end of the addition process, and the resulting anion 12b− is protonated during the workup. Thus, on the basis of the product distribution (Table 1), it can be postulated that at low temperatures \( k_{3b} < k_{7b} \) (entry 12) and at higher temperatures \( k_{3b} > k_{7b} \) (entry 11). At high t-BuLi/2b ratio, excess t-BuLi completely transforms 7b to anion 12b−, which subsequently gives 12b. Better understanding and support of this proposed mechanism require further detailed experimental studies.

Reaction of dibromide 2a and t-BuLi also gives the debrinated product 12a among unidentified product(s) arising presumably from the low stability of the [1,3]dioxane ring toward the base. The formation of 12a can be envisioned to occur in a way analogous to that of the generation of 12b from 2b. The initially formed anion 23a is protonated with t-BuBr to form 7a, which is further converted to 12a. In addition, some of the anion 23a apparently undergoes substitution reaction (CANS) with t-BuLi giving 10a (R = t-Bu). The distribution of these two products, 10a and 12a, indicates that \( k_{3a} > k_{6a} \). There is no clear evidence for the generation of carbene 22a, although it cannot be excluded that some of the unidentified byproduct(s) are derived from a reaction of t-BuLi with the transient bicyclo[1.1.0]butane 11a.

Overall, elimination of LiBr from anion 23a and the formation of carbene 22a (or a carbenoid) appears to be the slowest process among all possible pathways in the transformation of 2a, at least with MeLi and PhLi. The lithium salt 23a is stabilized by nearly 5 kcal/mol over salt 23b and appears to exhibit dual philicity: it reacts with electrophiles such as MeBr or, in their absence, with nucleophiles such as PhLi.

The origin of the observed difference in reactivity of the two cyclopropanes 2a and 2b lies primarily in the electronic structure of the carbones 22a and 22b and, to some extent, in the ability of the dioxane rings to chelate the Li+ ion. Analysis of the three carbones 22a−c shows significantly more electrophilic character of the dioxane carbene 22a due to the inductive effect of the −CH₂O− groups. This is evident from the higher positive charge of the carbenic center and lower energy of the LUMO. This in turn, results in tighter bonding to an electron donor Br−, as evident from the C−Br bond length in the anions 21 and Li salts 23, and less favorable α-elimination process in 21a and 23a. Consistent with this view is the observed slow addition of CBr₂ to olefin 3a, and also fast reactions of dibromide 2a with RLi (\( k_{3a} > k_{3b} \)), as compared to the cyclohexane analogues.

The rigidity of the molecular skeleton and the orientation of oxygen atoms relative to the carbenic center are not optimal for the effective chelation of Li⁺ in 23a. Therefore, this internal coordination provides only a modest additional enthalpic stabilization of 23a, which is compensated by the entropy decrease. It results, however, in moving the Li⁺ ion away from the carbanion center and exposing it to both electrophiles and nucleophiles. In other dibromocyclopropanes, containing either flexible or better aligned substituents, such as methoxy, alkoxymethyl, acetal, dialkylaminomethyl, the heteroatom can effectively chelate the Li⁺ ion increasing the overall stability of the salt and directing the insertion reaction. These single substituents, however, do not significantly affect the carbenic center, and the formation of carbones (carbenoids) and their subsequent reactions (insertion or rearrangement) are the dominant processes. This is in sharp contrast to our results for 2a, and, to our knowledge, there is no other dibromocyclopropane that is resistant to the carbone formation. In this sense dibromocyclopropane 2a is an exceptional compound.

Conclusions

The reactions of two dibromocyclopropanes 2a and 2b with three different organolithium reagents revealed several mecha

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organolithium. The cyclohexane derivative 2b reacts as expected to form carbene 22 (or carbodien), which undergoes rearrangement to 11b. In contrast, the anion derived from 2a is unusually stable and undergoes either alkylation with MeBr (electrophilic substitution) or arylation with PhLi (nucleophilic substitution) as the main or exclusive reaction pathways. This significant resistance to the α-elimination process in anion 23a is ascribed to the cumulative effect of four \(-\text{CH}_2\text{O}^-\) groups, rather than to the intramolecular coordination of the Li\(^{+}\) ion by the ring oxygen atoms. Calculations for a series of anions indicate that the dioxane ring increases the electrochemical character of the cyclopropyldiene by lowering the LUMO, which retards the α-elimination process. The effect is approximately additive for each dioxane group. A comparative analysis of the literature data indicates that a single \(-\text{CH}_2\text{O}^-\) or \(-\text{CH}_2\text{N}<\) substituent does not noticeably impact the reactivity of dibromocyclopropanes and their intermediates.

Overall, the electron withdrawing effect of the four \(-\text{CH}_2\text{O}^-\) groups results in the enhanced electrophilicity of carbene 22a and manifests itself in (i) the resistance of the anion 23a to the elimination of LiBr, (ii) slow addition of \(\text{CBr}_2\) to olefin 3a, and (iii) in fast reactions of dibromide 2a with RLi (\(k_{1a} > k_{1b}\)), as compared to the cyclohexane analogues.

Future studies of carbene 22a and its rearrangement to 1a and 11a will require a different precursor such as the appropriate diazo derivative.

Computational Details

Quantum-mechanical calculations were carried out with the B3LYP\(^{22}\) and MP2(fc)\(^{74}\) methods using the Gaussian 98 package.\(^{21}\) Geometry optimizations were performed with the DFT method using either the 6-31G(d,p) or 6-31G(d,p) (for NMR analysis) basis sets, appropriate symmetry constraints, and default convergence limits. Transition states were located using the QST3 keyword. The guess for the TS geometry was generated by convergence limits. Transition states were located using the QST3 method.\(^{75}\) Å for allene formation, and C1

Experimental Details

Melting points are uncorrected. NMR spectra were recorded at either 300 MHz (\(\text{H}\)) and 75 or 100 MHz (\(\text{C}\)), respectively, in CDCl\(_3\), unless otherwise specified. Chemical shifts were referenced to TMS (\(\text{H}\)) or solvent (\(\text{C}\)).

Reactivity of 13,13-Dibromo-2,4,9,11-tetraoxadispiro[5.0.5.1]tridecane (2a).

Method A. A 50% aq solution of NaOH (10 g, 125 mmol) was added dropwise at room temperature to a vigorously stirred solution of olefin 3a (3.45 g, 20 mmol), \(\text{CHBr}_3\) (5.5 mL, 60 mmol), and TEBA (50 mg, 0.2 mmol) in \(\text{CH}_2\text{Cl}_2\) (25 mL). After 12 h, no more progress was observed by GC/MS, and additional portions of CHBr3 (5 mL) and TEBA (50 mg) were added. The stirring was continued for 3 days during which two additional portions of CHBr3 and TEBA were added. The reaction mixture was filtered through Celite, which was washed with \(\text{CH}_2\text{Cl}_2\) (200 mL). The organic layer was separated, dried (NaSO\(_4\)), and concentrated. Excess CHBr3 was distilled off under reduced pressure. The resulting mixture of starting material and product (1:4 ratio by \(\text{H NMR}\)) was separated by column chromatography (CHCl3/EtOAc, 10:1). The isolated product (2.5 g) was recrystallized from EtOH, giving 1.80 g (33% yield) of 2a as colorless crystals (mp 162–166 °C). Alternatively, dibromide 2a was dried in vacuum (P\(_2\)O\(_5\)) and then sublimed at 125 °C 1.0 Torr giving a white solid: mp 163.5–164 °C; \(\text{H NMR}\) δ 3.99 and 4.04 (AB, \(J = 12.0\) Hz, 8H), 4.90 and 4.92 (AB, \(J = 6.2\) Hz, 4H); \(\text{13C NMR}\) δ 32.0, 40.7, 68.9, 94.1; IR (neat) 1147 \(\text{cm}^{-1}\); MS m/z 235 and 233 (1:1, 1), 86 (63), 65 (100); HRMS calcd for C\(_9\)H\(_{12}\)Br\(_2\)O\(_4\) 342.9181, found 342.9199. Anal. Calcd for C\(_9\)H\(_{11}\)Br\(_2\)O\(_4\): C, 31.63; H, 3.52. Found: C, 31.63; H, 3.50.

Method B. Following a general procedure,\(^{30}\) PhHgCBr\(_3\) (13.7 g, 26 mmol) was added in one portion to a stirred solution of olefin 3a (3.0 g, 17 mmol) in dry benzene (30 mL) under nitrogen. The reaction mixture was heated to 85 °C for 5 h. The solid precipitate was filtered, and the filtrate was concentrated. The resulting mixture of starting material 3a and product 2a (1:1 by \(\text{H NMR}\)) was separated as above giving 1.60 g (28% yield) of 2a.

13,13-Dibromodispiro[5.0.5.1]tridecane (2b).

The dibromide was obtained from olefin 3b as described for 2a in method A without additional portions of CHBr3 base or catalysts. The crude product was passed through a silica gel plug, recrystallized (isooctane), and sublimed (70 °C at 1 Torr) giving 71% yield of the dibromide 2b as colorless crystals: mp 101–102 °C; \(\text{H NMR}\) δ 1.37–1.74 (m); \(\text{13C NMR}\) δ 24.9, 25.8, 30.9, 35.3, 56.8; MS m/z 256 and 254 (M – Br, 1:1), 175 (M – 2 Br, 100). Anal. Calcd for C\(_{13}\)H\(_{17}\)Br\(_2\): C, 34.46; H, 6.00. Found: C, 34.51; H, 6.07.

Reaction of 2 with Organolithium. General Method. To a stirred solution of dibromide 2 (typically 0.7 mmol) in dry ether (50–70 mL), the appropriate amount of 1.2 M MeLi in ether, 2.0 M PhLi in dibutyl ether, or 1.7 M n-BuLi in pentane was added dropwise at –78, –10, or 36 °C under argon. After the addition was complete, the reaction mixture was placed in an ice–salt bath (–10 °C) or allowed to warm to ambient temperature. Alternatively, MeLi or PhLi were added to a solution of 2 in boiling ether. After 2 h, the reaction mixture was quenched with degassed water in free energy and used to calculate weighted shielding tensor for each nucleus, which was converted to NMR chemical shifts using cyclohexane as the reference. More details are listed in the Supporting Information.


(77) Gouding, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.; NBO version 3.1.

(0.25–0.5 mL), the aqueous layer was separated, and the organic
layer was concentrated. \(^1\)H NMR, \(^13\)C NMR, and GC/MS were
taken of the crude mixture. Products were purified and partially
separated by column chromatography and/or sublimation. Detailed
procedures and analytical data are provided in the Supporting
Information.

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**Supporting Information Available:** Full experimental details
for \(3–12\), NMR spectra for reaction products, and computational
results. This material is available free of charge via the Internet
at http://pubs.acs.org.

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