Syntheses of bicyclo[3.3.0]octanes and bicyclo[4.3.0]nonanes by ring expansion of isopropylidenecyclobutanes

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Abstract
When subjected to HBr/HOAc in polar solvents like acetic acid, 6-(1-methylethylidene)-bicyclo[3.2.0]heptanes undergo a ring expansion reaction yielding 2-bromo-3,3-dimethylbicyclo[3.3.0]octane and 3-bromo-2,2-dimethylbicyclo[3.3.0]octane. Several other isopropylidenecyclobutanes have been found to undergo the same reaction with high stereoselectivity and moderate regioselectivity. In less polar solvents like diethyl ether the ring expansion reaction is suppressed, and bromides resulting from addition of HBr to the isopropylidene double bond are obtained.

Keywords: Ring expansion reaction, HBr, acetic acid, isopropylidenecyclobutanes, bicyclo[3.3.0]octanes

Introduction
The bicyclo[3.3.0]octane and bicyclo[4.3.0]nonane skeletons are recognized as substructures of many biologically active, synthetically challenging compounds like capnellanes, hirsutanes and pastuereutins.1-7 Several other examples of ring expansions of four-membered carbocycles to give useful five-membered rings can be found in the literature.8-12 Despite several existing methods, the structural variety of these compounds still calls for new practical procedures to be developed.13 While working on a synthesis of the insect pheromone component lineatin, we found that the epoxide of 1 gave an acid catalysed ring expansion.14 Later we found that using HBr in acetic acid gave a near quantitative yield of the ring expanded product 2.15 The reaction was found to be both stereo- and regioselective as seen from both spectroscopic data and X-ray crystallography.
Scheme 1. Ring expansion reaction of 1.

Inspired by these results, we decided to investigate the reaction further. Such a regio- and stereoselective, high yielding reaction would be very useful in the syntheses of natural products, e.g. (±)-1-desoxyhypnophilin, a biologically active linear triquinane isolated from the East African mushroom Lentinus crinitus (L. ex Fr.) Fr.²

Scheme 2. Retrosynthetic analysis of (±)-1-desoxyhypnophilin.

In the present paper we would like to report a study in which several isopropylidenecyclobutane derivatives were tested for the ring expansion reaction.

Results and Discussion

The dibromomethylenecyclobutanes were prepared in excellent yields (81-87 %) by treatment of known ketones¹⁷-²⁰ with PPh₃ and CBr₄ in acetonitrile using a modified literature procedure.²¹ Acetonitrile was used since it has been found to be the best solvent for the reaction of ketones with PPh₃/CCl₄.²² The dibromomethylenecyclobutanes were then methylated twice with lithium dimethylecuprate.²¹ With low boiling products, the solvent was distilled at ambient pressure in order to minimise loss of product. The yields of the isopropylidenecyclobutanes were fairly good (50-67 %). In this way the isopropylidenecyclobutanes 4a-e were prepared. (Scheme 3 and Table 1).

Scheme 3. Preparation of the isopropylidenecyclobutanes 4a-e.
Table 1. Starting materials

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Dibromomethylene cyclobutane (isolated yield)</th>
<th>Isopropylidenecyclobutane (isolated yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Cyclobutane" /></td>
<td>3a (87%)</td>
<td>4a (60%)</td>
</tr>
<tr>
<td><img src="image" alt="Cyclobutane" /></td>
<td>3b (81%)</td>
<td>4b (60%)</td>
</tr>
<tr>
<td><img src="image" alt="Cyclobutane" /></td>
<td>3c (87%)</td>
<td>4c (67%)</td>
</tr>
<tr>
<td><img src="image" alt="Cyclobutane" /></td>
<td>3d (85%)</td>
<td>4d (50%)</td>
</tr>
<tr>
<td><img src="image" alt="Cyclobutane" /></td>
<td>3e (85%)</td>
<td>4e (62%)</td>
</tr>
</tbody>
</table>

Previous attempts in our group to achieve ring expansion of compound 1 using protic acids like HCl, p-toluene sulfonic acid or CF3COOH, and Lewis acids like BF3, AlCl3, HgSO4, Hg(OAc)2 or AgNO3 were unsuccessful. However, using 45% HBr in acetic acid a near quantitative yield of a product corresponding to compound 5 was achieved. When the reaction was carried out with 33% HBr in acetic acid at room temperature using the same amount of HBr (~8 eq.), a mixture of products were obtained.

![Scheme 4](image)

**Scheme 4.** Preparation of 5, 6 and 7.

The reactions were finished in 0.5-2 h and three products were observed. Two of these were ring expanded compounds 5 and 6. In addition variable amounts of 7 resulting from addition of HBr across the double bond, were also seen (Scheme 4). It was observed that 7 rearranged on the GLC, and for this reason it was not possible to give exact amounts of these compounds. The 1H NMR spectrum of the product mixture resulting when the alkene 4d was used as the substrate, indicated that the ratio of the ring expanded compounds (5d + 6d) to 7d was approximately 70:30, and that the ratio of 5d to 6d was 58:42 (1H NMR). Prolonged reaction times did not change the ratio 5d:6d. When substrate 4e was used, the ratio of the ring expanded compounds...
(5e+6e) to 7e was approximately 90:10. The gem-dimethyl singlets are easily detectable in the 1H NMR spectra of the product 7. So when none of these resonances were seen in the spectrum of the reaction mixture using 4a as substrate, this was clearly indicating that none or only small amounts of 7a could have been formed.

Attempts to isolate 5a and 6a by column chromatography failed since no separation was achieved, and separation of 5 and 6 by chromatography was not attempted. Instead analytical samples of 5 and 6 were isolated using preparative GLC.

Generally a high stereoselectivity was achieved. According to both 1H NMR and GLC analyses mainly one stereoisomer was formed, and only a few per cent of the other isomer could be detected. Representative examples are depicted in Table 2.

**Table 2.** Treatment of the isopropylidenecyclobutanes with excess 33 % HBr in acetic acid at room temperature

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Method</th>
<th>Ratio (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>4a</td>
<td>GLC</td>
<td>65</td>
</tr>
<tr>
<td>4a</td>
<td>NMR</td>
<td>64</td>
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<tr>
<td>4b</td>
<td>GLC</td>
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<tr>
<td>4c</td>
<td>GLC</td>
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<tr>
<td>4d</td>
<td>GLC</td>
<td>56</td>
</tr>
<tr>
<td>4d</td>
<td>NMR</td>
<td>58</td>
</tr>
<tr>
<td>4e</td>
<td>GLC</td>
<td>79</td>
</tr>
<tr>
<td>4e</td>
<td>NMR</td>
<td>74</td>
</tr>
</tbody>
</table>

<sup>a</sup> Conversion 100 %. Ratio based on GLC analyses (at full reaction time) and 1H NMR data (of the crude mixture).

The compounds 5, 6 and 7 are easily identified from their respective 1H NMR spectra. The 1H NMR spectra of 5 exhibited a characteristic doublet at δ 3-4 ppm due to the CH-Br signal. In the spectra of 6 the corresponding signal appeared as a doublet of doublet at δ 3.8-4.5 ppm. The compounds 7 could be identified from the two methyl singlets at δ 1.6-1.7 ppm consistent with a gem-dimethyl group situated on the same carbon atom as the bromine atom. The other features of the spectra were also in accord with the structures.

The rearrangement gave mainly one stereoisomer, but due to the flexibility of the two fused
5-membered rings it was not possible to use coupling constants to confirm which stereoisomer was predominantly formed. However, thorough analysis of the NMR spectra of 5a made it possible to distinguish the two protons on C4. A fairly strong interaction between the *endo* H4 proton and the α-proton (H2) based on the ROESY spectra could be seen, tentatively showing the stereochemistry of the bromine substituted carbon atom (H2) as depicted in Figure 1.

![Figure 1](image_url)

The regioselectivity, however, was only moderate and best for the isopropylidene-cyclobutane 4e, assumed to be the most strained substrate. The least strained substrate 4d yielded the lowest selectivity. With the substrates 4a and 4e only minor amounts (<10 %, GLC) of side products were observed. With the substrate 4d up to 18% side products were present (GLC), but some of them may result from decomposition of 7d in the injector. The substrates 4b and 4c, however, gave mixtures of several unidentified products where the ring expanded products 5 and 6, according to GLC analyses, constituted only small amounts. This was probably due to addition of HBr to the *endocyclic* double bond. Small amounts of two unidentified compounds could be isolated by preparative GLC from the complex mixture resulting from substrate 4b. The 1H NMR spectra indicated that no double bonds were present in these compounds, and no attempts were made to further elucidate the structures. The reaction mixture resulting from substrate 4c was so complex that separation was not attempted.

Changing the temperature of the reaction resulted in only minor effects. (Table 3) Both the stereo- and regioselectivity of the reaction was the same as at room temperature. Temperatures ranging from 0-5 °C to 70 °C were tried. For substrate 4d (entry 7), however, lowering the temperature to 0-5 °C slowed the ring expansion reaction down, and the major product was 7d (GLC) where the ring expansion had not taken place. The amounts of side products formed were approximately the same as at room temperature. Unfortunately, lowering the temperature did not affect the outcome of the reaction for the substrate 4c (entry 5), and a complex mixture containing only minor amounts of 5c and 6c resulted. Elevation of the temperature (entry 4) gave no trace of 5c and 6c.
Table 3. Temperature effects

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Temperature</th>
<th>Ratio (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<th>6</th>
<th>7</th>
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<tr>
<td>1</td>
<td>4a</td>
<td>70 °C</td>
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<td>65</td>
<td>35</td>
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<td>2</td>
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<td>50-60 °C</td>
<td></td>
<td>65</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>4a</td>
<td>0-5 °C</td>
<td></td>
<td>66</td>
<td>34</td>
<td>trace amounts</td>
</tr>
<tr>
<td>4</td>
<td>4c</td>
<td>50-60 °C</td>
<td></td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>5</td>
<td>4c</td>
<td>0-5 °C</td>
<td>small amounts&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>4d</td>
<td>50-60 °C</td>
<td></td>
<td>52</td>
<td>39</td>
<td>8&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>4d</td>
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<td></td>
<td>30</td>
<td>25</td>
<td>45&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Conversion 100 %. Ratio based on GLC data. <sup>b</sup>i.e. <15%<sup>c</sup>Rearranges to a certain extent on the GLC.

Since the temperature effects were minimal, changing the polarity of the reaction medium was tried. Representative results are presented in Table 4.

At first the reaction was performed using the same amount of HBr (in acetic acid) as before (~8 eq.). Using substrate 4a as a model, solvents with polarities ranging from hexane to CH₂Cl₂ were added in a ratio of HBr/HOAc : solvent, ~1:3 (e.g. entries 1 and 2). The regioselectivity did not improve. Moreover, using diethyl ether as the solvent, the ring expansion reaction was suppressed completely yielding 7a as the only product identified. Only minor amounts of side products (<10%) were observed. The reactions were performed at room temperature except for entry 6 (substrate 4c) that was performed in refluxing ether. Comparison of GLC chromatograms of the reactions of the bromide 4c at room temperature and at reflux, indicated that the temperature change only resulted in minor differences in the product ratio. Purification of 7a by preparative GLC or flash chromatography failed, and only the ring expanded products 5a and 6a were isolated. Even at direct injection on the MS, rearrangement of 7a was observed. The compound 7b gave a spectrum that was tentatively associated with the structure depicted for this compound, but for 7c and 7d no attempts to measure MS spectra were made since they all rearranged as easily as 7a.
Table 4. Solvent effects

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conditions</th>
<th>Ratio (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conversion (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>4a</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O, 1 h&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>4a</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;, 1 h&lt;sup&gt;b&lt;/sup&gt;</td>
<td>52 (58)</td>
<td>48 (42)</td>
</tr>
<tr>
<td>3</td>
<td>4a</td>
<td>Hexane, 1 h&lt;sup&gt;b&lt;/sup&gt;</td>
<td>(40)</td>
<td>(28)</td>
</tr>
<tr>
<td>4</td>
<td>4a</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O, 4 h&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
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<td>4b</td>
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<td>-</td>
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<td>4c</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O, Δ, 22 h&lt;sup&gt;c,d,e&lt;/sup&gt;</td>
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<td>-</td>
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<td>7</td>
<td>4d</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O, 8 h&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ratio based on <sup>1</sup>H NMR data or GLC data (in parenthesis), conversion based on GLC data.
<sup>b</sup> HBr/HOAc: solvent, ∼1:3;  
<sup>c</sup> HBr/HOAc: solvent, ∼1:20;  
<sup>d</sup> Slow addition of HBr in acetic acid;  
<sup>e</sup> Reaction performed at reflux

When the reaction was performed in diethyl ether using an excess of only 2-4 eq. of HBr (HBr/HOAc:ether, ∼1:20) (entries 4 to 7) no change in the outcome of the reaction was observed; the ring expansion reaction was suppressed for all the substrates, and only 7 were obtained. No attempts were made to purify 7b-d since the purification of 7a failed. The compound 7c was not isolated, but merely identified from the <sup>1</sup>H NMR spectrum of the crude product by resonances at δ ~1.6-1.7 ppm corresponding to the gem-dimethyl group situated on the bromine substituted carbon atom, a singlet at δ 1.85 ppm corresponding to the vinylic methyl group and a multiplet at 5.27-5.37 ppm (alkene proton). Signals due to formation of the rearranged bromides 5c and 6c could not be seen in the spectrum. The yields of the products 7a-7d have not been optimized.

Slower addition of the HBr/HOAc solution resulted only in a slower reaction, and in accordance with literature, an excess of 2-3 eq. of HBr was necessary to complete the reaction.

The stereochemistry of the bromides 7 was difficult to establish, but the ROESY spectrum of 7b shows a strong coupling between the two bridgehead protons H1 and H5, and a weaker coupling between the bridgehead proton H5 and the α-proton (H6). Molecular models (ball-and-stick models) indicate that due to the rigidity of this bicyclic compound, the coupling between protons H5 and H1 and between protons H5 and H6 should be of similar strength if the α-proton (H6) and the bridgehead protons are syn. This indicates that 7b has the stereochemistry depicted in Figure 2 with the (CH<sub>3</sub>)<sub>2</sub>CBr-group situated exo. This is confirmed by the ROESY spectrum.
revealing correlations between the (CH$_3$)$_2$CBr-group and both the bridgehead proton H5 and the exo H7 proton.

**Figure 2**

Finally, attempts to achieve ring expansion on 7b and 7c were made treating them with acetic acid at elevated temperatures. The substrate 7b yielded the ring expanded compounds 5b and 6b in moderate regioselectivity. The substrate 7c gave a complex mixture containing moderate amounts of 5c and 6c (Table 5 and Scheme 5).

**Scheme 5.** Ring expansion of 7 in HOAc.

**Table 5.** Ring expansion of HBr adducts

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reaction time (h)</th>
<th>Ratio (%)</th>
<th>Method</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7b</td>
<td>1.5</td>
<td>71 29</td>
<td>GLC</td>
<td>96$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>72 28</td>
<td>NMR</td>
<td>90$^b$</td>
</tr>
<tr>
<td>7c</td>
<td>8</td>
<td>63 37</td>
<td>GLC</td>
<td>89$^a$</td>
</tr>
</tbody>
</table>

$^a$ Conversion based on GLC data. $^b$ Conversion based on $^1$H NMR data.

The reaction gave an impure mixture, and the $^1$H NMR spectrum of this was too complex to indicate the conversion of 7c or the ratio of 5c and 6c formed. On the other hand, the crude mixture obtained from 7b gave consisting results, when analysed by GLC and NMR, both with respect to conversion of the starting material and the ratio of 5b to 6b. This information is
indicative of both the conversion of 7c and the ratio of 5c and 6c, although the bromide 7c has been found to rearrange on the GLC.

Preparative GLC yielded analytical samples of 5b, 6b and 5c. For 6c an impure sample was obtained, and 6c was merely identified from the $^1$H NMR spectrum of this sample by the singlets at δ 0.96 and 1.16 ppm (the gem-dimethyl groups), a multiplet at δ 1.69-1.77 ppm (alkene CH$_3$ group), a doublet of doublet at δ 4.11 ppm (CHBr proton, $J$ 5.4 and 5.9 Hz) and a multiplet at δ 5.25-5.35 ppm (alkene proton).

A possible mechanism of the ring expansion reaction is depicted in Scheme 6.

![Scheme 6. Possible mechanism of the ring expansion reaction.](image)

The initially formed tertiary carbocation can rearrange through either pathway a or b yielding 5 or 6, respectively. This mechanism fails to explain the high stereoselectivity exhibited by the reaction, however. Sterical congestion alone cannot explain the high stereoselectivity, and possibly a cage type mechanism is at work.

When the reaction was performed with the isopropylidenecyclobutane 1, a higher regioselectivity was reported. This may be due to the fact that if substrate 1 were to undergo a ring expansion reaction by pathway b, a severely sterically congested bromide with adjacent gem-dimethyl substituted carbon atoms would result. However, the mechanism of the reaction was not studied.
Experimental Section

General. Melting points were measured on an Electrothermal 9100 apparatus. IR was performed on a Perkin Elmer Paragon 500 FT-IR spectrophotometer or a Magna-IR 550 Nicolet FT-IR spectrophotometer. Only selected absorption bands in IR are reported. The routine NMR spectra were recorded on a Varian Gemini 200 instrument or Bruker DPX 200, DPX 300 or DRX 500 instruments using CDCl$_3$ as a solvent and TMS as a reference. $^1$H NMR spectra were recorded at 200, 300 and 500 MHz, and $^{13}$C NMR spectra were recorded at 50, 75 and 125 MHz. MS spectra were recorded on a JEOL DX-303 mass spectrometer, and HRMS spectra were recorded on a Fisons VG ProSpec Q mass spectrometer using electronic ionisation (EI) at an ionisation potential of 70 eV unless otherwise stated. Only selected peaks in MS are reported. Analytical GLC was carried out on a Varian 3400 gas chromatograph and a Chrompack CP9001 gas chromatograph using Chrompack WCOT fused silica capillary columns (25 m, i.d. 0.32 mm, CP-sil-8 CB 1.20 µm), and preparative GLC was carried out on a Varian 3300 and a Varian 3400 gas chromatograph using a 10% SP-2100 packed column (2.5 m, i.d. 4 mm). Analytical thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kieselgel 60 F$_{254}$. Compounds were visualized by UV light and/or stained with p-anisaldehyde solutions followed by heating. Flash column chromatography was performed on silicagel (Merck Kieselgel 60, (0,040-0,063 mm, 230-400 Mesh ASTM). All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. When required, the solvents were dried (by standard procedures) and distilled and the reactions performed under an atmosphere of nitrogen. Anhydrous solvents purchased in sure seal bottles over molecular sieves were used without further drying.

Bicyclo[3.2.0]heptan-6-one, bicyclo[3.2.0]hept-2-en-6-one, bicyclo[4.2.0]octan-7-one and 2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-one were prepared from the corresponding dichloroketene adducts according to literature. 4-Methylbicyclo[3.2.0]hept-3-en-6-one was prepared from 3-hydroxy-3-methyl-6-heptenoic acid according to literature procedures.

Typical procedure for the preparation of the (dibromomethylene)bicyclic compounds. A mixture of triphenylphosphine (24.13 g, 92.0 mmol) and bicyclo[3.2.0]heptan-6-one (1.983 g, 18.0 mmol) in acetonitrile (140 mL) was cooled to 0 °C, and CBr$_4$ (15.22 g, 45.9 mmol) was added in one portion. The mixture was stirred at room temperature under nitrogen for 4 h. Solid material was removed by vacuum filtration, and the solvent was removed in vacuo. The residue was dissolved in a minimal quantity of dichloromethane and added dropwise to hexane (dichloromethane:hexane:1:5). Precipitated solid was filtered and washed with hexane. Solvents were removed in vacuo, and the procedure was repeated twice. Purification of the residue by chromatography (silica, hexane) yielded the pure dibromomethylencyclobutane 3a (4.16 g, 87%) as a colourless oil. IR (film) ($v_{max}$, cm$^{-1}$): 2952 (s, shoulder), 2858 (m), 1660 (w), 1444 (w), 1413 (w), 840 (m) and 799 (s). $^1$H NMR (200 MHz, CDCl$_3$): $\delta_H$ 1.30-1.88 (5H, m), 1.88-2.10 (2H, m), 2.53-2.73 (2H, m) and 3.10-
3.24 (1H, m). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta_{C}$ 24.6 (CH$_2$), 29.9 (CH$_2$), 31.7 (CH), 32.5 (CH$_2$), 36.7 (CH$_2$), 49.4 (CH), 79.1 (C) and 148.6 (C). MS, m/z (%) = 264 (M$^+$, 10)/266 (M$^+$, 22)/268 (M$^+$, 9), 236 (13)/238 (22)/240 (12), 185 (30)/187 (29), 157 (17)/159 (16), 106 (82), 105 (100), 79 (39), 77 (40), 51 (43) and 39 (53). HRMS: C$_8$H$_{10}$$_7$Br$_8$ requires m/z = 265.9129. Found m/z = 265.9132.

6-(Dibromomethylene)bicyclo[3.2.0]hept-2-ene (3b). Triphenylphosphine (10.25 g, 39.1 mmol), bicyclo[3.2.0]hept-2-en-6-one $^{18,24}$ (0.830 g, 7.68 mmol), CBr$_4$ (6.495 g, 19.6 mmol), acetonitrile (30 mL). The dibromomethylene cyclobutane 3b (1.64 g, 81%) was obtained as a colourless oil. IR (CDCl$_3$) ($\nu_{\text{max}}$, cm$^{-1}$): 3056 (m), 2948 (s, shoulder), 2852 (m), 1747 (m, br), 1713 (m, br), 1665 (m, br), 1607 (m, br), 848 (s) and 802 (s). $^1$H NMR (200 MHz, CDCl$_3$): $\delta$H 2.24 (1H, dt, $J_{16.5}$ and 3.4 Hz), 2.43-2.62 (1H, m), 2.66-2.84 (2H, m), 3.14-3.30 (1H, m), 3.32-3.46 (1H, m) and 5.70-5.80 (2H, m).

$^{13}$C NMR (50 MHz, CDCl$_3$): $\delta_{C}$ 36.4 (CH$_2$), 39.3 (CH), 39.8 (CH$_2$), 46.2 (CH), 80.9 (C), 131.7 (CH), 132.2 (CH) and 149.8 (C). MS, m/z (%) = 262 (M$^+$, 31)/264 (M$^+$, 58)/266 (M$^+$, 29), 247 (16)/249 (29)/251 (15), 183 (92)/185 (92), 104 (97), 103 (100), 77 (56), 66 (98) and 51 (60). HRMS: C$_8$H$_{10}$$_7$Br$_8$ requires m/z = 263.8972. Found m/z = 263.8979.

7-(Dibromomethylene)-2-methylbicyclo[3.2.0]hept-2-ene (3c). Triphenylphosphine (24.13 g, 92.0 mmol), 4-methylbicyclo[3.2.0]hept-3-en-6-one $^{19,26}$ (2.199 g, 18.0 mmol), CBr$_4$ (15.22 g, 45.9 mmol), acetonitrile (140 mL). The dibromomethylene cyclobutane 3c (4.33 g, 87%) was obtained as a colourless oil. IR (film) ($\nu_{\text{max}}$, cm$^{-1}$): 2937 (w), 2967 (s), 2908 (s), 2847 (m), 1660 (w, br), 1442 (m), 1413 (m), 1117 (m), 840 (m) and 788 (s). $^1$H NMR (200 MHz, CDCl$_3$): $\delta$H 1.79-1.87 (3H, m), 2.09-2.37 (2H, m), 2.44-2.63 (1H, m), 2.63-2.87 (2H, m), 3.59-3.73 (1H, m) and 5.33-5.42 (1H, m).

$^{13}$C NMR (50 MHz, CDCl$_3$): $\delta_{C}$ 17.1 (CH$_3$), 31.0 (CH), 39.6 (CH$_2$), 46.2 (CH), 80.9 (C), 131.7 (CH), 132.2 (CH) and 149.8 (C). MS, m/z (%) = 276 (M$^+$, 23)/278 (M$^+$, 44)/280 (M$^+$, 22), 261 (16)/263 (30)/265 (14), 248 (8)/250 (15)/252 (8), 197 (31)/199 (30), 118 (100), 117 (90), 80 (35) and 79 (33). HRMS: C$_9$H$_{10}$$_7$Br$_8$ requires m/z = 277.9129. Found m/z = 277.9127.

7-(Dibromomethylene)bicyclo[4.2.0]octane (3d). Triphenylphosphine (24.13 g, 92.0 mmol), bicyclo[4.2.0]octan-7-one $^{19,25}$ (2.235 g, 18.0 mmol), CBr$_4$ (15.22 g, 45.9 mmol), acetonitrile (150 mL). The dibromomethylene cyclobutane 3d (4.27 g, 85%) was obtained as a colourless oil. IR (film) ($\nu_{\text{max}}$, cm$^{-1}$): 2933 (s), 2855 (m), 1665 (w), 1600 (w, br), 1442 (m), 1413 (m), 1117 (m), 840 (m) and 788 (s). $^1$H NMR (200 MHz, CDCl$_3$): $\delta$H 1.13-1.60 (5H, m), 1.60-1.90 (3H, m), 2.15-2.45 (2H, m), 2.45-2.68 (1H, m) and 2.75-3.00 (1H, m).

$^{13}$C NMR (50 MHz, CDCl$_3$): $\delta_{C}$ 21.6 (CH$_2$), 21.8 (CH$_2$), 24.1 (CH$_2$), 26.6 (CH), 26.9 (CH$_2$), 37.9 (CH$_2$), 43.4 (CH), 77.3 (C) and 148.8 (C). MS, m/z (%) = 278 (M$^+$, 23)/278 (M$^+$, 49)/280 (M$^+$, 100)/282 (M$^+$, 50), 250 (12)/252 (23)/254 (12), 246 (8)/248 (16)/240 (8), 224 (9)/226 (17)/228 (8), 199 (19)/201 (23), 119 (32), 91 (20) and 67 (22). HRMS: C$_9$H$_{12}$$_7$Br$_8$ requires m/z = 279.9285. Found m/z = 279.9288.

1-(Dibromomethylene)-2,2a,7,7a-tetrahydro-1H-cyclobuta[a]indene (3e). Triphenylphosphine (8.973 g, 34.2 mmol), 2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-one $^{18,24}$ (1.063 g, 6.72 mmol), CBr$_4$ (5.683 g, 17.1 mmol), acetonitrile (56 mL). The dibromomethylene cyclobutane 3e
(1.79 g, 85%) was obtained as a white solid, mp. 105-108 °C. IR (CCl₄) (ν_max, cm⁻¹): 3073 (w), 3024 (w), 2929 (m), 2852 (w), 1661 (w), 837 (s) and 798 (s). ¹H NMR (200 MHz, CDCl₃): δ_H 2.42 (1H, dt, J 16.7 and 3.4 Hz), 3.05 (1H, dd, J 16.7 and 8.4 Hz), 3.18 (1H, dd, J 17.2 and 9.1 Hz), 3.36-3.52 (1H, m), 3.56-3.72 (1H, m), 3.74-3.88 (1H, m) and 7.16-7.32 (4H, m). ¹³C NMR (50 MHz, CDCl₃): δ_C 36.2 (CH₂), 39.3 (CH), 41.3 (CH₂), 47.5 (CH), 81.4 (C), 124.3 (CH), 124.6 (CH), 126.5 (CH), 126.6 (CH), 142.8 (C), 144.4 (C) and 147.9 (C). MS, m/z (%) = 312 (M⁺, 8)/314 (M⁺, 14)/316 (M⁺, 8), 233 (8)/235 (8), 154 (16), 153 (25), 152 (14), 117 (11), 116 (100) and 115 (29). HRMS: C₁₂H₁₀Br₂ requires m/z = 311.9149. Found m/z = 311.9143.

Typical procedure for the preparation of the isopropylidene bicyclic compounds using a modified literature procedure

6-(1-Methylethylidene)bicyclo[3.2.0]heptane (4a). An ethereal solution of lithium dimethylcuprate was prepared at 0 °C by suspending CuI (15.36 g, 80.7 mmol) in dry diethyl ether (80 mL) and adding a 1.5 M solution of MeLi in diethyl ether until the mixture was colourless. To this solution 3a (2.178 g, 8.19 mmol) in dry diethyl ether (96 mL) was added, and the mixture was stirred at room temperature overnight. Then methyl iodide (24 mL) was added dropwise under cooling (ice/water), and stirring was continued at room temperature for 1 h. Saturated aq ammonium chloride was carefully added, and the aqueous phase was extracted with ether (3x). The combined etheral extracts were washed with brine and dried (Na₂SO₄). For solids: The solvents were removed in vacuo, and the crude material was purified by chromatography (silica, hexane). For liquids: The solvent was removed by careful distillation at ambient pressure and finally by flushing with N₂ while cooled (ice-water). The residue was distilled bulb-to-bulb at 0.7 mmHg and an oil bath temperature of 40 °C slowly rising to 70 °C, yielding the isopropylidenecyclobutane 4a (0.665 g, 60%) as a colourless oil. IR (film) (ν_max, cm⁻¹): 2948 (s), 2922 (s), 2851 (m), 1446 (m, shoulder) and 1369 (m). ¹H NMR (200 MHz, CDCl₃): δ_H 1.44 (3H, s), 1.51 (3H, s), 1.20-1.80 (6H, m), 1.85-2.08 (1H, m), 2.52-2.74 (2H, m) and 3.13-3.30 (1H, m). ¹³C NMR (50 MHz, CDCl₃): δ_C 18.7 (CH₃), 19.0 (CH₃), 25.2 (CH₂), 32.5 (CH₂), 33.5 (CH, CH₂), 33.6 (CH₂), 46.0 (CH), 122.4 (C) and 133.4 (C). MS, m/z (%) = 136 (M⁺, 70), 121 (100), 107 (57), 94 (43), 93 (88), 79 (52), 67 (70) and 41 (36). HRMS: C₁₀H₁₆ requires m/z = 136.1252. Found m/z = 136.1247.

6-(1-Methylethylidene)bicyclo[3.2.0]hept-2-ene (4b). CuI (10.77 g, 56.6 mmol) in dry diethyl ether (70 mL), 1.6 M methylithium in diethyl ether and 3b (1.510 g, 5.72 mmol) in dry diethyl ether (70 mL). MeI (17 mL). The isopropylidenecyclobutene 4b (0.457 g, 60%) was obtained as a colourless oil. IR (film) (ν_max, cm⁻¹): 3047 (m), 2967 (m), 2918 (s), 2849 (m), 1609 (w), 1444 (m) and 1369 (m). ¹H NMR (300 MHz, CDCl₃): δ_H 1.45 (3H, s), 1.55 (3H, s), 2.20-2.34 (1H, m), 2.36-2.65 (2H, m), 2.70-2.91 (1H, m), 3.12-3.32 (1H, m), 3.35-3.55 (1H, m) and 5.68-5.87 (2H, m). ¹³C NMR (50 MHz, CDCl₃): δ_C 19.0 (CH₃), 19.3 (CH₃), 36.4 (CH₂), 38.9 (CH₂), 41.2 (CH), 43.0 (CH), 124.9 (C), 130.6 (CH), 133.4 (CH) and 135.0 (C). MS, m/z (%) = 134 (M⁺, 58), 119
Typical methods for the preparation of the bromobicyclo[3.3.0]octanes, the bromobicyclo[4.3.0]nonanes, and the HBr adducts (7)

Method A: 2-Bromo-3,3-dimethylbicyclo[3.3.0]octane (5a) and 3-bromo-2,2-dimethylbicyclo[3.3.0]octane (6a)

A solution of 4a (0.191 g, 1.40 mmol) in 33% HBr in acetic acid (1.83 mL, 10.4 mmol) was stirred at room temperature for 1 h. Diethyl ether (25 mL) and water (10 mL) was added. The organic layer was separated, and the water phase was extracted with diethyl ether (3 × 5 mL). The combined etheral phases were washed with water (10 mL), saturated aq NaHCO₃ (10 mL), brine (10 mL) and dried (MgSO₄). Evaporation of the solvent gave a mixture (Crude yield: 0.277 g, 91%) consisting of 5a (64%) and 6a (36%) according to NMR and GLC. Analytical samples of 5a and 6a were obtained by preparative GLC.

2-Bromo-3,3-dimethylbicyclo[3.3.0]octane (5a). IR (ATR) (ν_max, cm⁻¹): 2949 (s, shoulder), 2864 (s), 1458 (m), 1445 (m), 1385 (m), 1368 (m), 1382 (m), 1335 (m) and 752 (m). ¹H NMR (500 MHz,
CDCl$_3$: $\delta$H 0.90-1.00 (1H, m), 0.98 (6H s, 2 × CH$_3$), 1.28-1.37 (1H, m), 1.39-1.63 (5H, m), 1.87 (1H, dd, J 12.7 and 8.9 Hz), 2.49-2.60 (1H, m), 2.67-2.76 (1H, m) and 3.40 (1H, d, J 9.5 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$C 22.7 (CH$_3$), 24.4 (CH$_2$), 26.2 (CH$_3$), 30.6 (CH$_2$), 33.0 (CH$_2$), 39.5 (CH), 44.1 (C), 44.8 (CH$_2$), 52.3 (CH) and 69.3 (CH). MS, $m/z$ (%) = 216 (M$^+$, 5)/218 (M$^+$, 4), 138 (14), 137 (100), 121 (7), 95 (35), 81 (71), 79 (15), 69 (50), 67 (22), 55 (17) and 41 (23). HRMS: C$_{10}$H$_{17}$Br requires $m/z = 216.0514$. Found $m/z = 216.0504$.

3-Bromo-2,2-dimethylbicyclo[3.3.0]octane (6a). $^1$H NMR (200 MHz, CDCl$_3$): $\delta$H 0.97 (3H, s), 0.98 (3H, s), 0.85-1.42 (3H, m), 1.46-1.72 (2H, m), 1.75-2.34 (4H, m), 2.37-2.60 (1H, m) and 3.94 (1H, d, J 10.1 Hz) and 5.48-5.64 (2H, m). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$C 23.1 (CH$_3$), 26.2 (CH$_3$), 28.0 (CH$_2$), 30.1 (CH$_2$), 35.7 (CH$_2$), 39.2 (CH), 42.6 (CH$_2$), 44.6 (C), 52.5 (CH) and 61.0 (CH). MS, $m/z$ (%) = 216 (M$^+$, 3)/218 (M$^+$, 3), 148 (5)/150 (5), 138 (16), 137 (100), 121 (9), 110 (100), 95 (59), 81 (75), 69 (94) and 67 (68). HRMS: C$_{10}$H$_{17}$Br requires $m/z = 216.0514$. Found $m/z = 216.0512$.

Method B: 6-Bromo-7,7-dimethylbicyclo[3.3.0]oct-2-ene (5b) and 7-bromo-6,6-dimethylbicyclo[3.3.0]oct-2-ene (6b). A solution of 7b (0.127 g, 0.590 mmol) in acetic acid (0.13 mL, 2.26 mmol) was stirred for 1.5 h at 70 °C and worked up as in method A yielding a mixture (crude yield: 0.096 g, 76%) that contained 5b (65%), 6b (25%) and 7b (10%) ($^1$H NMR). Analytical samples of 5b and 6b were obtained by preparative GLC.

6-Bromo-7,7-dimethylbicyclo[3.3.0]oct-2-ene (5b). IR (ATR) ($\nu_{max}$, cm$^{-1}$): 3050 (m), 2956 (s), 2923 (s), 2852 (s), 2853 (m), 1460 (m, shoulder), 1384 (m), 1368 (m), 810 (m) and 724 (s). $^1$H NMR (200 MHz, CDCl$_3$): $\delta$H 1.00 (3H, s), 1.02 (3H, s), 1.14 (1H, dd, J 12.7 and 8.2 Hz), 1.96 (1H, d, J 11.2 and 7.2 Hz). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$C 23.7 (CH$_3$), 27.0 (CH$_3$), 37.2 (CH$_2$), 43.8 (CH$_2$), 44.2 (C), 47.2 (CH), 49.7 (CH), 70.1 (CH), 127.1 (CH) and 133.7 (CH). MS, $m/z$ (%) = 214 (M$^+$, 33)/216 (M$^+$, 32), 199 (11)/201 (10), 173 (43)/175 (41), 135 (67), 119 (24), 107 (42), 93 (55), 91 (34), 79 (100) and 77 (38). HRMS: C$_{10}$H$_{15}$Br requires $m/z = 214.0357$. Found $m/z = 214.0361$.

7-Bromo-6,6-dimethylbicyclo[3.3.0]oct-2-ene (6b). IR (ATR) ($\nu_{max}$, cm$^{-1}$): 2956 (m), 2923 (s), 2852 (s), 1464 (m), 1456 (m), 804 (m) and 724 (m). $^1$H NMR (200 MHz, CDCl$_3$): $\delta$H 0.75-1.10 (1H, m), 1.00 (3H, s), 1.04 (3H, s), 1.87-2.65 (4H, m), 3.10-3.30 (1H, m), 3.90 (1H, d, J 10.1 and 7.0 Hz) and 5.48-5.64 (2H, m). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$C 23.3 (CH$_3$), 26.4 (CH$_3$), 35.0 (CH$_2$), 41.0 (CH$_2$), 45.3 (C), 47.3 (CH), 49.4 (CH), 61.5 (CH), 129.7 (CH) and 132.6 (CH). MS, $m/z$ (%) = 214 (M$^+$, 7)/216 (M$^+$, 7), 135 (32), 119 (12), 107 (15), 93 (28), 91 (18), 79 (23), 77 (18), 69 (72), 66 (100) and 41 (33). HRMS: C$_{10}$H$_{15}$Br requires $m/z = 214.0357$. Found $m/z = 214.0347$.

8-Bromo-2,7,7-trimethylbicyclo[3.3.0]oct-2-ene (5c) and 7-bromo-2,8,8-trimethylbicyclo[3.3.0]oct-2-ene (6c). Preparation according to Method B: 0.261 g of a crude mixture containing mainly the bromide 7c was added acetic acid (0.30 mL, 5.21 mmol) and stirred at 50 °C for 2.5 h. Since GLC analysis indicated that 37% of 7c still remained, more acetic acid (0.30 mL, 5.21 mmol) was added. The mixture was stirred for another 3.5 h at 50 °C and for 2 h at 60 °C and...
worked up as in Method A. An impure mixture (0.183 g) containing moderate amounts of 5c and 6c was obtained. An analytical sample of 5c was obtained by preparative GLC. Attempts to isolate other components in the mixture failed.

8-Bromo-2,7,7-trimethylbicyclo[3.3.0]oct-2-ene (5c). IR (ATR) (ν\text{max}, \text{cm}^{-1}): 3036 (w), 2957 (s), 2931 (s), 2894 (m), 2850 (s), 1455 (m), 1384 (m), 1369 (m), 798 (m), 794 (m) and 752 (m). \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}): δ\text{H} 1.00 (3H, s), 1.02 (3H, s), 0.90-1.20 (1H, m), 1.81 (3H, br s), 1.94 (1H, dd, J 12.4 and 8.4 Hz), 1.65-2.10 (1H, m), 2.38-2.60 (1H, m), 2.70-2.94 (1H, m), 3.11-3.30 (1H, m), 3.53 (1H, d, J 7.9 Hz) and 5.11-5.21 (1H, m). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}): δ\text{C} 15.7 (CH\textsubscript{3}), 23.8 (CH\textsubscript{3}), 26.4 (CH\textsubscript{3}), 38.5 (CH\textsubscript{2}), 39.1 (CH), 44.6 (C), 46.6 (CH\textsubscript{2}), 62.6 (CH), 67.5 (CH), 123.7 (CH) and 140.3 (C). MS, m/z (%) = 228 (M\textsuperscript{+}, 16)/230 (M\textsuperscript{+}, 18), 149 (7), 148 (15), 133 (23), 93 (100), 91 (41), 79 (43), 77 (37), 41 (47) and 39 (24). HRMS: C\textsubscript{11}H\textsubscript{17}Br requires m/z = 228.0514. Found m/z = 228.0514.

7-Bromo-8,8-dimethylbicyclo[4.3.0]nonane (5d), 8-bromo-7,7-dimethylbicyclo[4.3.0]nonane (6d) and 7-(1-bromo-1-methylethyl)bicyclo[4.2.0]octane (7d). Preparation according to Method A. Isopropylidenecyclobutane 4d (0.210 g, 1.40 mmol) and 33% HBr in acetic acid (1.83 mL, 10.4 mmol) was stirred at room temperature for 2 h. Work-up as in Method A yielded an impure mixture (0.316 g) containing (5d + 6d) to 7d in a ratio of 70 : 30. (\textsuperscript{1}H NMR). The ratio of 5d to 6d was 58:42. (\textsuperscript{1}H NMR). Analytical samples of 5d and 6d were obtained by preparative GLC. The bromide 7d was identified by GLC analysis and comparison with a \textsuperscript{1}H NMR spectrum of a sample of 7d prepared by using ether as the solvent (\textit{vide infra}).

7-Bromo-8,8-dimethylbicyclo[4.3.0]nonane (5d). IR (ATR) (ν\text{max}, \text{cm}^{-1}): 2951 (s), 2925 (s), 2856 (s), 2856 (s), 1459 (m), 1448 (m), 1387 (w), 1366 (m), 802 (m) and 795 (m). \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}): δ\text{H} 1.03 (3H, s), 1.09 (3H, s), 0.85-2.10 (11H, m), 2.11-2.35 (1H, m) and 3.97 (1H, d, J 11.7 Hz). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}): δ\text{C} 20.7 (CH\textsubscript{2}), 24.7 (CH\textsubscript{2}), 24.8 (CH\textsubscript{2}), 28.2 (CH\textsubscript{3}), 30.5 (CH\textsubscript{2}), 35.3 (CH), 40.6 (C), 45.2 (CH), 45.4 (CH\textsubscript{2}) and 67.1 (CH). MS, m/z (%) = 230 (M\textsuperscript{+}, 12)/232 (M\textsuperscript{+}, 13), 151 (100), 135 (23), 109 (13), 95 (73), 81 (30), 69 (49), 67 (25) and 41 (32). HRMS: C\textsubscript{11}H\textsubscript{19}Br requires m/z = 230.0670. Found m/z = 230.0671.

8-Bromo-7,7-dimethylbicyclo[4.3.0]nonane (6d). IR (ATR) (ν\text{max}, \text{cm}^{-1}): 2975 (s), 2930 (s), 2852 (s), 1463 (m), 1448 (m), 1387 (w), 1366 (m), 802 (m) and 655 (m). \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}): δ\text{H} 0.94 (3H, s), 1.07 (3H, s), 0.70-1.35 (3H, m), 1.35-1.75 (6H, m), 2.00-2.35 (2H, m), 2.40-2.70 (1H, m) and 4.23 (1H, dd, J 9.4 and 7.6 Hz). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}): δ\text{C} 21.4 (CH\textsubscript{2}), 22.5 (CH\textsubscript{3}), 25.0 (CH\textsubscript{2}), 25.5 (CH\textsubscript{2}), 27.2 (CH\textsubscript{3}), 27.9 (CH\textsubscript{2}), 34.6 (CH), 39.3 (CH\textsubscript{2}), 46.7 (C), 47.1 (CH) and 62.5 (CH). MS, m/z (%) = 230 (M\textsuperscript{+}, 12)/232 (M\textsuperscript{+}, 13), 151 (100), 135 (23), 109 (13), 95 (73), 81 (30), 69 (49), 67 (25) and 41 (32). HRMS: C\textsubscript{11}H\textsubscript{19}Br requires m/z = 230.0670. Found m/z = 230.0671.

1-Bromo-2,2-dimethyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene (5e) and 2-bromo-1,1-dimethyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene (6e) and 1-(1-bromo-1-methylethyl)-2,2a,7,7a-tetrahydro-1H-cyclobuta[a]indene (7e). Preparation according to Method A. Isopropylidenecyclobutane 4e (0.217 g, 1.18 mmol) in 33% HBr in acetic acid (1.53 mL, 8.72 mmol) was stirred at room temperature for 1 h and worked up as in Method A yielding a mixture
(crude yield: 0.292 g, 94%) consisting of 5e + 6e (90%) and 7e (10%) (1H NMR). The ratio of 5e to 6e was 74:26 (1H NMR). Analytical samples of 5e and 6e were obtained by preparative GLC.

1-Bromo-2,2-dimethyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene (5e). IR (ATR) (νmax, cm⁻¹): 3072 (w), 3022 (s, br), 2958 (s, shoulder), 2868 (m), 2851 (m), 1482 (s), 1459 (s), 1447 (m), 1386 (s), 1372 (m), 807 (s) and 751 (s). 1H NMR (200 MHz, CDCl3): δH 1.03 (3H, s), 1.13 (3H, s), 1.48 (1H, dd, J 12.9 and 7.2 Hz), 2.36 (1H, dd, J 12.8 and 9.9 Hz), 2.81-3.05 (1H, m), 3.05-3.35 (2H, m), 3.57 (1H, d, J 10.1 Hz), 3.73 (1H, q, J 7.3 Hz) and 7.07-7.27 (4H, m).

13C NMR (50 MHz, CDCl3): δC 24.0 (CH3), 26.9 (CH3), 36.2 (CH2), 44.7 (C), 45.1 (CH2), 46.4 (CH), 50.7 (CH), 68.9 (CH), 124.1 (CH), 124.8 (CH), 126.3 (CH), 126.5 (CH), 140.8 (C) and 146.8 (C). MS, m/z (%) = 264 (M+), 185 (32), 169 (11), 155 (21), 141 (30)/143 (30), 129 (100), 128 (93), 116 (36), 115 (76), 91 (19), 69 (31) and 41 (43). HRMS: C14H17Br requires m/z = 264.0514. Found m/z = 264.0519.

2-Bromo-1,1-dimethyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene (6e). IR (ATR) (νmax, cm⁻¹): 3072 (w), 3022 (w), 2958 (s), 2928 (s, shoulder), 2868 (m), 2851 (m), 1482 (s), 1459 (s), 1447 (m), 1386 (s), 1372 (m), 807 (s) and 751 (s). 1H NMR (200 MHz, CDCl3): δH 0.99 (3H, s), 1.13 (3H, s), 2.18-2.36 (1H, m), 2.48-2.70 (1H, m), 2.72-2.90 (2H, m), 2.90-3.10 (1H, m), 3.70-3.86 (1H, m), 3.97 (1H, dd, J 9.4 and 7.0 Hz) and 7.10-7.19 (4H, m).

13C NMR (50 MHz, CDCl3): δC 23.0 (CH3), 26.5 (CH3), 34.6 (CH2), 43.2 (CH2), 45.7 (C), 47.3 (CH), 50.7 (CH), 61.9 (CH), 123.6 (CH), 123.73 (CH), 126.1 (CH), 126.2 (CH), 142.4 (C) and 145.9 (C). MS, m/z (%) = 264 (M+), 185 (14), 141 (16)/143 (18), 129 (29), 128 (31), 116 (82), 115 (80), 69 (100) and 41 (37). HRMS: C14H17Br requires m/z = 264.0514. Found m/z = 264.0525.

6-(1-Bromo-1-methylethyl)bicyclo[3.2.0]heptane (7a). Typical procedure: To a solution of isopropylidenecyclobutane 4a (0.051 g, 0.374 mmol) in diethyl ether (3 mL) was added 33% HBr in acetic acid (0.20 mL, 1.14 mmol), and the mixture was stirred at room temperature for 4 h. The mixture was worked up as in Method A above yielding crude bromide 7a (0.040 g, 49%). 1H NMR (200 MHz, CDCl3): δH 1.36-1.60 (5H, m), 1.65 (3H, s), 1.67 (3H, s), 1.63-1.94 (3H, m), 1.97-2.13 (1H, m) and 2.42-2.68 (2H, m).

13C NMR (75 MHz, CDCl3): δC 25.8 (CH2), 28.4 (CH2), 31.3 (CH3), 31.4 (CH3), 33.3 (CH2), 33.4 (CH), 33.6 (CH2), 42.5 (CH), 51.7 (CH) and 73.2 (C).

6-(1-bromo-1-methylethyl)bicyclo[3.2.0]hept-2-ene (7b). Typical procedure: To a solution of 4b (0.185 g, 1.38 mmol) in diethyl ether (8 mL) was added 33% HBr in acetic acid (0.27 mL, 1.54 mmol), and the mixture was heated at reflux overnight. Since 19% of 4b was left according to GLC, more 33% HBr in acetic acid (0.03 mL, 0.171 mmol) was added, and the mixture was refluxed for 7 h. Then the mixture was worked up as in Method A, yielding crude 7b (0.224 g, 76%). 1H NMR (300 MHz, CDCl3): δH 1.62 (3H, s), 1.66 (3H, s), 1.70-1.88 (1H, m), 1.97-2.28 (3H, m), 2.45-2.62 (1H, m), 2.82 (1H, q, J 7.1 Hz), 2.95-3.10 (1H, m) and 5.65-5.83 (2H, m). 13C NMR (75 MHz, CDCl3): δC 30.2 (CH2), 31.2 (CH3), 31.4 (CH3), 40.01 (CH), 40.05 (CH2), 40.4 (CH), 54.0 (CH), 72.2 (C), 130.5 (CH) and 134.2 (CH). MS, m/z (%) = 214 (M+, 41)/216 (M+, 37), 175 (16), 135 (69), 134 (28), 119 (24), 107 (24), 105 (24), 93 (33), 79 (38), 77 (26), 69 (42) and 66 (100).
7-(1-Bromo-1-methylethyl)bicyclo[3.2.0]hept-2-ene (7c). To a solution of isopropylidenecyclobutane 4c (0.210 g, 1.42 mmol) in diethyl ether (7 mL) was added 33% HBr in acetic acid (0.29 mL, 1.65 mmol), and the mixture was heated at reflux for 12h. GLC indicated that 37% of 4c still remained, and more 33% HBr in acetic acid (0.06 mL, 0.342 mmol) was added. The mixture was stirred for another 5.5 h at reflux. There was still 17% of 4c left, and more 33% HBr in acetic acid (0.06 mL, 0.342 mmol) was added. The mixture was stirred for another 4 h at reflux (still 6% of 4c left) and worked up as in Method A yielding a crude mixture (0.278 g) containing mainly 7c (NMR). The crude product was used without further purification.

7-(1-Bromo-1-methylethyl)bicyclo[4.2.0]octane (7d). To a solution of isopropylidenecyclobutane 4d (0.030 g, 0.200 mmol) in diethyl ether (2 mL) was added 33% HBr in acetic acid (0.07 mL, 0.399 mmol), and the mixture was stirred for 1h at room temperature. As there was still 58% of 4d left, more 33% HBr in acetic acid (0.04 mL, 0.228 mmol) was added, and the mixture was stirred for another 5 h. Still 9% of 4d remained, and more 33% HBr in acetic acid (0.04 mL, 0.228 mmol) was added. The mixture was stirred for 1h (8% of 4d left) when more 33% HBr in acetic acid (0.01 mL, 0.057 mmol) was added, and finally the mixture was stirred for another 1h. In total 4.6 equivalents of HBr were added (0.160 mL, 0.912 mmol), and the total reaction time was 8 h. Work-up as in Method A above yielded the bromide 7d (crude yield: 0.028 g, 61%). 1H NMR (200 MHz, CDCl3): δH 0.74-2.12 (11H, m), 1.67 (3H, s), 1.68 (3H, s), 2.22-2.40 (1H, m) and 2.40-2.58 (1H, m). 13C NMR (50 MHz, CDCl3): δC 22.1(CH2), 23.6 (CH2), 26.8 (CH2), 27.4 (CH), 29.8 (CH2), 30.0 (CH2), 31.8 (CH3), 32.2 (CH3), 36.2 (CH), 49.3 (CH) and 73.0 (C).

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