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

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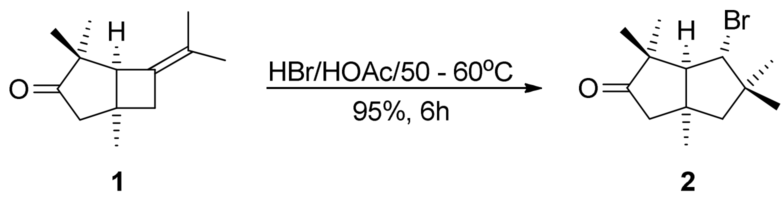
Abstract
When subjected to HBr/HOAc in polar solvents like acetic acid, 6-(1-methylethylidene)-bicyclo[3.2.0]heptanes undergo a ring expansion reaction yielding 2-bromo-3,3-dimethylbicyclo[3.3.0]octane and 3-bromo-2,2-dimethylbicyclo[3.3.0]octane. Several other isopropylidenecyclobutanes have been found 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

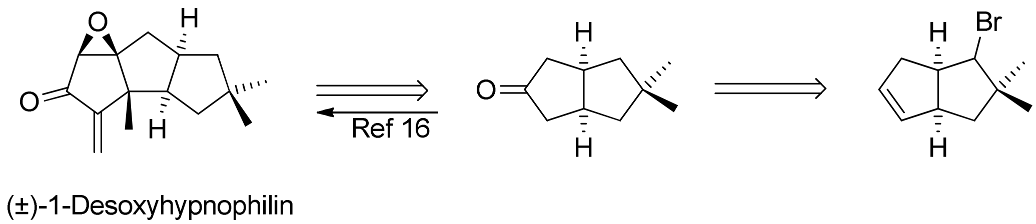
Introduction

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 pasteurestins.[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.[1]

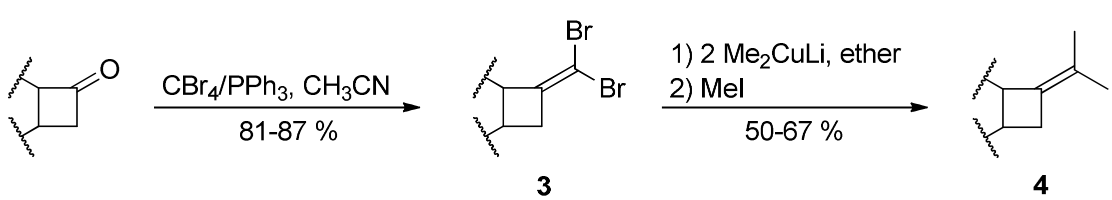


Scheme 2. Retrosynthetic analysis of (±)-1-desoxyhypnophilin.

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

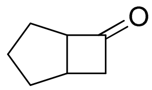
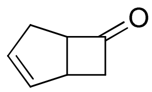
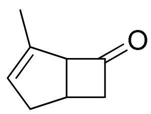
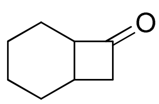
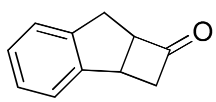
Results and Discussion

The dibromomethylenecyclobutanes were prepared in excellent yields (81-87 %) by treatment of known ketones[17-20] with PPh_3 and CBr_4 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 PPh_3/CCl_4.[22] The dibromomethylenecyclobutanes were then methylated twice with lithium dimethylcuprate.[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).

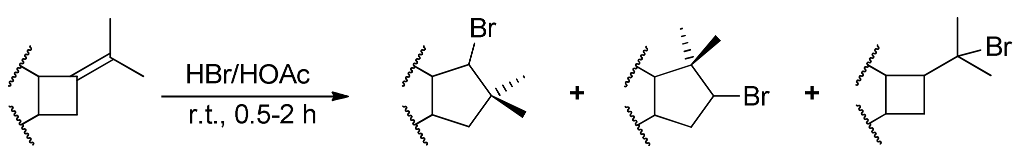


Scheme 3. Preparation of the isopropylidenecyclobutanes **4a-e**.

Table 1. Starting materials

Substrate	Dibromomethylenecyclobutane (isolated yield)	Isopropylidenecyclobutane (isolated yield)
	**3a** (87%)	**4a** (60%)
	**3b** (81%)	**4b** (60%)
	**3c** (87%)	**4c** (67%)
	**3d** (85%)	**4d** (50%)
	**3e** (85%)	**4e** (62%)

Previous attempts in our group to achieve ring expansion of compound **1** using protic acids like HCl, *p*-toluenesulfonic acid or CF_3COOH, and Lewis acids like BF_3, $AlCl_3$, $HgSO_4$, $Hg(OAc)_2$ or $AgNO_3$ were unsuccessful.[15] 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.



4 **5** **6** **7**

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 ^{1}H 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 (^{1}H 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 ^{1}H 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 ^{1}H 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

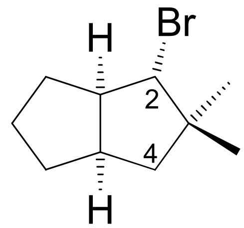
Substrate	Method	Ratio (%)^{a}	
		5	**6**
4a	GLC	65	35
4a	NMR	64	36
4b	GLC	small amounts	small amounts
4c	GLC	small amounts	small amounts
4d	GLC	56	44
4d	NMR	58	42
4e	GLC	79	21
4e	NMR	74	26

[a] Conversion 100 %. Ratio based on GLC analyses (at full reaction time) and ^{1}H NMR data (of the crude mixture).

The compounds **5**, **6** and **7** are easily identified from their respective ^{1}H NMR spectra. The ^{1}H 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.



5a

Figure 1

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 ^{1}H 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

Entry	Substrate	Temperature	Ratio (%)[a]		
			5	**6**	**7**
1	**4a**	70 °C	65	35	-
2	**4a**	50-60 °C	65	35	-
3	**4a**	0-5 °C	66	34	trace amounts
4	**4c**	50-60 °C	-	-	-
5	**4c**	0-5 °C	small amounts[b]	small amounts[b]	small amounts[b]
6	**4d**	50-60 °C	52	39	8[c]
7	**4d**	0-5 °C	30	25	45[c]

[a] Conversion 100 %. Ratio based on GLC data. [b] i. e. <15%
[c] 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 CH_2Cl_2 were added in a ratio of HBr/HOAc : solvent, ~1:3 (eg. 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

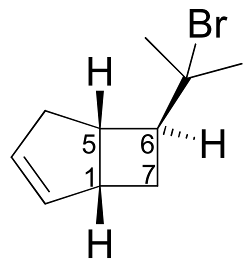
Entry	Substrate	Conditions	Ratio (%)[a]			Conversion (%)[a]
			5	**6**	**7**	
1	**4a**	Et_2O, 1 h[b]	-	-	~100	~100
2	**4a**	CH_2Cl_2, 1 h[b]	52 (58)	48 (42)	-	100
3	**4a**	Hexane, 1 h[b]	(40)	(28)	(32)	95
4	**4a**	Et_2O, 4 h[c]	-	-	~100	94
5	**4b**	Et_2O, 3 h[c]	-	-	~100	100
6	**4c**	Et_2O, Δ, 22 h[c,d,e]	-	-	major	94
7	**4d**	Et_2O, 8 h[c,d]	-	-	~100	91

[a] Ratio based on ^{1}H NMR data or GLC data (in parenthesis), conversion based on GLC data.
[b] HBr/HOAc: solvent, ~1:3; [c] HBr/HOAc: solvent, ~1:20; [d] Slow addition of HBr in acetic acid;
[e] 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 ^{1}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,[23] an excess of 2-3 eq. of HBr was necessary to complete the reaction.

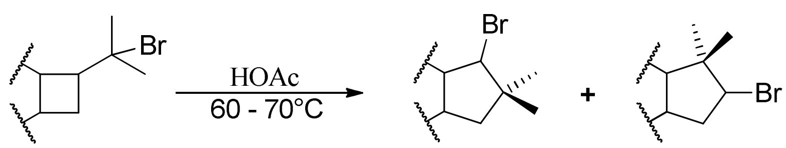
The stereochemistry of the bromides **7** was difficult to establish, but the ROESY spectrum of **7b** shows a strong coupling between the two bridgehead protons H1 and H5, and a weaker coupling between the bridgehead proton H5 and the α-proton (H6). Molecular models (ball-and-stick models) indicate 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 $(CH_3)_2$CBr-group situated *exo*. This is confirmed by the ROESY spectrum revealing correlations between the $(CH_3)_2CBr$-group and both the bridgehead proton H5 and the *exo* H7 proton.



7b

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

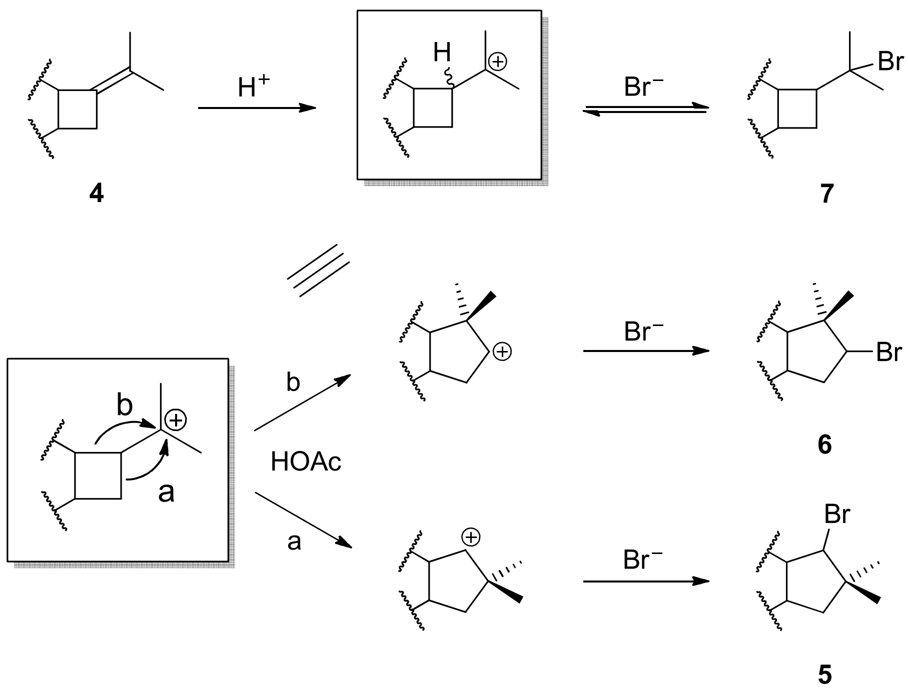
Substrate	Reaction time (h)	Ratio (%)		Method	Conversion (%)
		5	**6**		
7b	1.5	71	29	GLC	96[a]
		72	28	NMR	90[b]
7c	8	63	37	GLC	89[a]

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

The reaction gave an impure mixture, and the ^1H 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.

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.[15] 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,[17] bicyclo[3.2.0]hept-2-en-6-one,[18] bicyclo[4.2.0]octan-7-one[20] and 2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]inden-1-one[18] were prepared from the corresponding dichloroketene adducts according to literature.[24,25] 4-Methylbicyclo[3.2.0]hept-3-en-6-one[19] was prepared from 3-hydroxy-3-methyl-6-heptenoic acid according to literature procedures.[26]

Typical procedure for the preparation of the (dibromomethylene)bicyclic compounds[21,22]

6-(Dibromomethylene)bicyclo[3.2.0]heptane (**3a**). A mixture of triphenylphosphine (24.13 g, 92.0 mmol) and bicyclo[3.2.0]heptan-6-one[17,24] (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 dibromomethylenecyclobutane **3a** (4.16 g, 87%) as a colourless oil. IR (film) ($\nu_{max,}$ cm^{-1}): 2952 (s, shoulder), 2858 (m), 1660 (w), 1444 (w), 1413 (w), 840 (m) and 799 (s). ^{1}H NMR (200 MHz, $CDCl_3$): δ_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, $CDCl_3$): δ_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: $C_8H_{10}{}^{79}Br^{81}Br$ 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 dibromomethylenecyclobutane **3b** (1.64 g, 81%) was obtained as a colourless oil. IR ($CDCl_3$) (ν_{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, $CDCl_3$): δ_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, $CDCl_3$): δ_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: $C_8H_8{}^{79}Br^{81}Br$ 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 dibromomethylenecyclobutane **3c** (4.33 g, 87%) was obtained as a colourless oil. IR (film) (ν_{max}, cm^{-1}): 3037 (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, $CDCl_3$): δ_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, $CDCl_3$): δ_C 17.1 (CH_3), 31.0 (CH), 39.6 (CH_2), 39.9 (CH_2), 60.5 (CH), 78.0 (C), 125.8 (CH), 138.7 (C) and 148.8 (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: $C_9H_{10}{}^{79}Br^{81}Br$ 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[20,25] (2.235 g, 18.0 mmol), CBr_4 (15.22 g, 45.9 mmol), acetonitrile (150 mL). The dibromomethylenecyclobutane **3d** (4.27 g, 85%) was obtained as a colourless oil. IR (film) (ν_{max}, cm^{-1}): 2933 (s), 2855 (m), 1665 (w), 1449 (m, shoulder) and 802 (m, shoulder). ^{1}H NMR (200 MHz, $CDCl_3$): δ_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, $CDCl_3$): δ_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^+, 49)/280 (M^+, 100)/282 (M^+, 50), 250 (12)/252 (23)/254 (12), 236 (8)/238 (16)/240 (8), 224 (9),/226 (17)/228 (8), 199 (19)/201 (23), 119 (32), 91 (20) and 67 (22). HRMS: $C_9H_{12}{}^{79}Br^{81}Br$ requires *m/z* = 279.9285. Found *m/z* = 279.9288.

1-(Dibromomethylene)-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]indene (3e). Triphenylphosphine (8.973 g, 34.2 mmol), 2,2a,7,7a-tetrahydro-1*H*-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 dibromomethylenecyclobutane **3e**

(1.79 g, 85%) was obtained as a white solid, mp. 105-108 °C. IR (CCl_4) (ν_{max}, cm^{-1}): 3073 (w), 3024 (w), 2929 (m), 2852 (w), 1661 (w), 1480 (w), 837 (w) and 798 (s). ^1H NMR (200 MHz, $CDCl_3$): 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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 36.2 (CH_2), 39.3 (CH), 41.3 (CH_2), 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: $C_{12}H_{10}{}^{79}Br_2$ 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[21]

6-(1-Methylethylidene)bicyclo[3.2.0]heptane (4a). An etheral 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 (Na_2SO_4). 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 N_2 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, $CDCl_3$): 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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 18.7 (CH_3), 19.0 (CH_3), 25.2 (CH_2), 32.5 (CH_2), 33.5 (CH, CH_2), 33.6 (CH_2), 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: $C_{10}H_{16}$ 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 methyllithium 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, $CDCl_3$): 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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 19.0 (CH_3), 19.3 (CH_3), 36.4 (CH_2), 38.9 (CH_2), 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

(62), 105 (20), 92 (56), 91 (99), 79 (21), 78 (30), 77 (20), 68 (23), 67 (41), 66 (100), 41 (31) and 39 (34). HRMS: $C_{10}H_{14}$ requires *m/z* = 134.1096. Found *m/z* = 134.1089.

2-Methyl-7-(1-methylethylidene)bicyclo[3.2.0]hept-2-ene (4c). CuI (15.36 g, 80.7 mmol) in dry diethyl ether (80 mL), 1.6 M methyllithium in diethyl ether and **3c** (2.268 g, 8.16 mmol) in dry diethyl ether (96 mL). MeI (24 mL). The isopropylidenecyclobutene **4c** (0.814 g, 67%) was obtained as a colourless oil. IR (film) (ν_{max}, cm^{-1}): 3034 (w), 2963 (s), 2909 (s), 2848 (s), 1648 (w), 1445 (m) and 1373 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 1.47 (3H, s), 1.62 (3H, s), 1.73 (3H, br s), 2.02-2.36 (2H, m), 2.43-2.65 (1H, m), 2.65-2.86 (2H, m), 3.60-3.73 (1H, m) and 5.25-5.34 (1H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 16.4 (CH_3), 18.9 (CH_3), 19.4 (CH_3), 32.6 (CH), 36.2 (CH_2), 39.9 (CH_2), 57.3 (CH), 121.0 (C), 123.8 (CH), 134.6 (C) and 141.0 (C). MS, *m/z* (%) = 148 (M^+, 93), 133 (100), 106 (52), 105 (100), 92 (59), 91 (66), 80 (53), 79 (49) and 41 (40). HRMS: $C_{11}H_{16}$ requires *m/z* = 148.1252. Found *m/z* = 148.1254.

7-(1-Methylethylidene)bicyclo[4.2.0]octane (4d).[27] CuI (15.36 g, 80.7 mmol) in dry diethyl ether (80 mL), 1.6 M methyl lithium in diethyl ether and **3d** (2.285 g, 8.16 mmol) in dry diethyl ether (96 mL). MeI (24 mL).The isopropylidenecyclobutane **4d** (0.610 g, 50%) was obtained as a colourless oil, and the spectral data were in accordance with the literature.[27]

1-(1-Methylethylidene)-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]indene (4e). CuI (10.48 g, 55.0 mmol) in dry diethyl ether (60 mL), 1.6 M methyl lithium in diethyl ether, **3e** (1.749 g, 5.57 mmol) in dry diethyl ether (60 mL) and MeI (17 mL). The isopropylidenecyclobutane **4e** (0.633 g, 62%) was obtained as a white solid, mp. 42-45 °C. IR (CCl_4) (ν_{max}, cm^{-1}): 3070 (w), 3022 (w), 2924 (s, br), 2851 (m), 1479 (m), 1450 (m) and 1371 (w). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 1.41 (3H, br s), 1.60 (3H, br s), 2.32-2.50 (1H, m), 2.95-3.27 (3H, m), 3.57-3.82 (2H, m) and 7.07-7.26 (4H, m). ^{13}C (50 MHz, $CDCl_3$): δ_C 19.1 (CH_3), 19.3 (CH_3), 37.7 (CH_2), 38.5 (CH_2), 41.2 (CH), 44.1 (CH), 124.2 (CH), 124.5 (CH), 125.1 (C), 125.9 (CH), 126.1 (CH), 133.4 (C), 143.6 (C) and 146.6 (C). MS, *m/z* (%) = 184 (M^+, 40), 141 (27), 128 (16), 117 (12), 116 (100), 115 (45), 73 (11) and 41 (18). HRMS: $C_{14}H_{16}$ requires *m/z* = 184.1252. Found *m/z* = 184.1252.

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-dimethyl-bicyclo[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 $NaHCO_3$ (10 mL), brine (10 mL) and dried ($MgSO_4$). 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), 802 (m) and 752 (m). ^{1}H NMR (500 MHz,

$CDCl_3$): δ_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, $CDCl_3$): δ_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: $C_{10}H_{17}{}^{79}Br$ requires *m/z* = 216.0514. Found *m/z* = 216.0504.

3-Bromo-2,2-dimethylbicyclo[3.3.0]octane (6a). ^1H NMR (200 MHz, $CDCl_3$): δ_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, dd, *J* 11.2 and 7.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ_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: $C_{10}H_{17}{}^{79}Br$ 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-dimethyl-bicyclo[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%) (^1H 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) (ν_{max}, cm^{-1}): 3050 (m), 2956 (s), 2923 (s), 2853 (m), 1460 (m, shoulder), 1384 (m), 1368 (m), 810 (m) and 724 (s). ^1H NMR (200 MHz, $CDCl_3$): δ_H 1.00 (3H, s), 1.02 (3H, s), 1.14 (1H, dd, *J* 12.7 and 8.2 Hz), 1.96 (1H, dd, *J* 12.7 and 9.3 Hz), 2.15-2.35 (1H, m), 2.45-2.70 (1H, m), 2.85-3.05 (1H, m), 3.05-3.25 (1H, m), 3.48 (1H, d, *J* 10.1 Hz) and 5.48-5.64 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ_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: $C_{10}H_{15}{}^{79}Br$ requires *m/z* = 214.0357. Found *m/z* = 214.0361.

7-Bromo-6,6-dimethylbicyclo[3.3.0]oct-2-ene (6b). IR (ATR) (ν_{max}, cm^{-1}): 2956 (m), 2922 (s), 2852 (s), 1464 (m), 1456 (m), 804 (m) and 724 (m). ^1H NMR (200 MHz, $CDCl_3$): δ_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, dd, *J* 10.1 and 7.0 Hz) and 5.47-5.67 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ_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: $C_{10}H_{15}{}^{79}Br$ 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_{max}, cm^{-1}): 3036 (w), 2957 (s), 2931 (s), 2894 (m), 2850 (s), 1455 (m), 1443 (m), 1384 (m), 1369 (m), 798 (m), 794 (m) and 752 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ_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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 15.7 (CH_3), 23.8 (CH_3), 26.4 (CH_3), 38.5 (CH_2), 39.1 (CH), 44.6 (C), 46.6 (CH_2), 62.6 (CH), 67.5 (CH), 123.7 (CH) and 140.3 (C). MS, *m/z* (%) = 228 (M^+, 16)/230 (M^+, 18), 149 (7), 148 (15), 133 (23), 93 (100), 91 (41), 79 (43), 77 (37), 41 (47) and 39 (24). HRMS: $C_{11}H_{17}{}^{79}Br$ 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. (^{1}H NMR). The ratio of **5d** to **6d** was 58:42. (^{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 ^{1}H NMR spectrum of a sample of **7d** prepared by using ether as the solvent (*vide infra*).

7-Bromo-8,8-dimethylbicyclo[4.3.0]nonane (5d). IR (ATR) (ν_{max}, cm^{-1}): 2951 (s), 2925 (s), 2856 (s), 1459 (m), 1448 (m), 1387 (w), 1366 (m), 802 (m), 795 (m) and 734 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ_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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 20.7 (CH_2), 24.7 (CH_2), 24.8 (CH_2), 28.2 (CH_3), 29.3 (CH_3), 30.5 (CH_2), 35.3 (CH), 40.6 (C), 45.2 (CH), 45.4 (CH_2) and 67.1 (CH). MS, *m/z* (%) = 230 (M^+, 12)/232 (M^+, 13), 151 (100), 135 (23), 109 (13), 95 (73), 81 (30), 69 (49), 67 (25) and 41 (32). HRMS: $C_{11}H_{19}{}^{79}Br$ requires *m/z* = 230.0670. Found *m/z* = 230.0671.

8-Bromo-7,7-dimethylbicyclo[4.3.0]nonane (6d). IR (ATR) (ν_{max}, cm^{-1}): 2975 (s), 2930 (s), 2852 (s), 1463 (m), 1455 (m), 1387 (m), 1366 (m), 809 (m) and 655 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ_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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 21.4 (CH_2), 22.5 (CH_3), 25.0 (CH_2), 25.5 (CH_2), 27.2 (CH_3), 27.9 (CH_2), 34.6 (CH), 39.3 (CH_2), 46.7 (C), 47.1 (CH) and 62.5 (CH). MS, *m/z* (%) = 230 (M^+, 1)/232 (M^+, 1), 151 (34), 135 (11), 124 (20), 109 (17), 95 (50), 81 (23), 69 (100), 67 (48), 55 (29) and 41 (73). HRMS: $C_{11}H_{19}{}^{79}Br$ requires *m/z* = 230.0670. Found *m/z* = 230.0667.

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-1*H*-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%) (^{1}H NMR). The ratio of **5e** to **6e** was 74:26 (^{1}H 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) (ν_{max}, cm^{-1}): 3072 (w), 3022 (m), 2958 (s, br), 2928 (s, shoulder), 2868 (m), 2851 (m), 1482 (s), 1459 (s), 1447 (m), 1386 (m), 1372 (m), 807 (s) and 751 (s). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 24.0 (CH_3), 26.9 (CH_3), 36.2 (CH_2), 44.7 (C), 45.1 (CH_2), 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^+, 31)/266 (M^+, 30), 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: $C_{14}H_{17}{}^{79}Br$ 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) (ν_{max}, cm^{-1}): 3070 (w), 3021 (w), 2964 (s), 2934 (s), 2870 (m), 2852 (w), 1482 (m), 1459 (m), 1385 (m), 1368 (m), 835 (w) and 750 (s). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 23.0 (CH_3), 26.5 (CH_3), 34.6 (CH_2), 43.2 (CH_2), 45.7 (C), 47.3 (CH), 50.7 (CH), 61.9 (CH), 123.69 (CH), 123.73 (CH), 126.1 (CH), 126.2 (CH), 142.4 (C) and 145.9 (C). MS, *m/z* (%) = 264 (M^+, 11)/266 (M^+, 13), 185 (14), 141 (16)/143 (18), 129 (29), 128 (31), 116 (82), 115 (80), 69 (100) and 41 (37). HRMS: $C_{14}H_{17}{}^{79}Br$ 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%). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 1.36-1.60 (5H, m), 1.65 (3H, s), 1.67 (3H, s), 1.63-1.94 (3H, m), 1.95-2.13 (1H, m) and 2.42-2.68 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 25.8 (CH_2), 28.4 (CH_2), 31.3 (CH_3), 31.4 (CH_3), 33.3 (CH_2), 33.4 (CH), 33.6 (CH_2), 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%). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 30.2 (CH_2), 31.2 (CH_3), 31.4 (CH_3), 40.01 (CH), 40.05 (CH_2), 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)-2-methylbicyclo[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%). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 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). ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 22.1(CH_2), 23.6 (CH_2), 26.8 (CH_2), 27.4 (CH), 29.8 (CH_2), 30.0 (CH_2), 31.8 (CH_3), 32.2 (CH_3), 36.2 (CH), 49.3 (CH) and 73.0 (C).

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