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Bromination of norbornene derivatives: synthesis of brominated norbornanes and norbornenes

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Abstract

The low and high temperature bromination of 7-bromobicyclo[2.2.1]hept-2-ene and 2,7-dibromobicyclo[2.2.1]hept-2-ene were studied and the possible role of a neighboring group participation in rearrangements was investigated. The formation mechanism of the isomers as well as the role of the substituent on the rearrangement were discussed. The structure elucidation of the formed compounds was achieved by NMR spectral data; particularly, the γ-*gauche* effect was discussed in connection with the configuration of the bromine atoms.

Keywords: Norbornene; Non-classical carbocation; Bromination; Wagner–Meerwein rearrangement; γ-*gauche* Effect

1. Introduction

Electrophilic bromination of simple olefins has been extensively studied within the last two decades. In general, the reaction is stereoselective and leads to *trans*-1,2-dibromides via a three-membered bromonium intermediate.[1–6] The bromination of unsaturated bicyclic systems with molecular bromine is generally complex.[7–11] For this reason, bromination of bridged olefins has attracted a good deal of attention for a long time. Highly brominated compounds, such as pesticides, plastics, fire-retardants, and pharmaceutical chemicals,[12–16] have numerous industrial applications and they also play an important role as key compounds for the synthesis of other derivatives.[17–21]

Great interest has been focused on the halogenation of norbornene (**1**),[22,23] norbornadiene (**2**),[24–30] and benzonorbornadiene (**3**)[31–40] derivatives. Norbornadiene (**2**) and benzonorbornadiene (**3**) have homoallylic diene systems, but in the later one, one of the double bonds is incorporated in a benzene ring. Therefore, comparison of these systems in view of the bromination reactions is important.

In a previous study we showed that the bromination of norbornadiene **2** with molecular bromine at low temperature results in the formation of rearranged products **4**–**6**[26] whereas benzonorbornadiene **3** gives a single rearranged product **7**[36] (Scheme 1). Norbornadiene (**2**) has a homoallylic diene system. Therefore, it is clear that this rearrangement process is supported by the vinyl-bromonium ion interaction to give mainly cyclopropanoid dibromides **5** and **6**. In addition to this, Caple and co-workers[40] and we[32] showed that bromination of 7-bromobenzonorbornadiene (**8**) gives tribromide **9** in quantitative yield (Scheme 1). The exclusive formation of the *cis-exo*-tribromide **9** can be explained by the formation of a symmetrical *non*-classical carbocation during the Wagner–Meerwein rearrangement. This reaction clearly demonstrates that even in a case where a bulky group such as a bromine atom located over the double bond in **8**, the *exo*-selectivity is not affected during the addition of bromine.

In this paper, we were interested in the synthesis of the bromides **10** and **11** and their bromination reactions (Fig. 1). The

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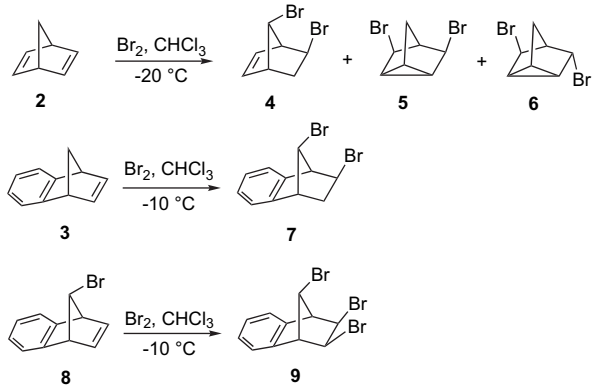


Scheme 1.

bromine atom in **10** blocks the *exo*-face of the double bond. Therefore, we were interested to see in which extent the σ-bond participation will take place compared with the benzo-derivative **8**. On the other hand, how the bromine atom attached to the double bond in **11** can affect the mode of the reaction.

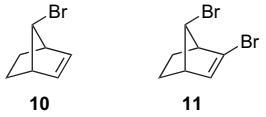
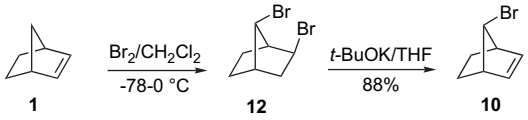


Figure 1.

2. Results and discussion

The synthesis of the monobromide **10** was accomplished as described in the literature.[23,41] Norbornene (**1**) was subjected to bromination reaction at −78 °C to afford the rearranged dibromide **12** as the major product, which was separated by column chromatography. Treatment of the crude product with 4 equiv of potassium *tert*-butoxide in THF gave an 88% yield of **10** (Scheme 2).



Scheme 2.

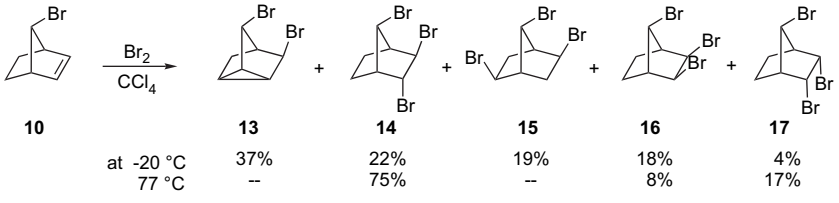
Firstly, the bromination of **10** was investigated at low temperature. The electrophilic addition of bromine to **10** was carried out in carbon tetrachloride at −20 °C. The ^{1}H NMR spectral studies of the crude product revealed the formation of five isomeric products. Crystallization and column chromatography allowed us to isolate the products **13**, **14**, **15**, **16**, and **17** in 37, 22, 19, 18, and 4% yields, respectively (Scheme 3).

In the course of studying the bromination reactions over the last two decades we noticed that the reaction temperature has a dramatic influence on the product distribution.[7–11,31–40,42–45] This factor encouraged us to raise the bromination temperature higher in order to search for the ratio of *non*-rearranged bromination products derived from **10**. A hot solution of bromine in CCl_4 was added directly to the refluxing solution of **10** in CCl_4. The NMR analysis of the crude product indicated that the reaction mixture consisted of three products. After column chromatography, three isomeric compounds; *trans*-tribromide **14**, *exo-cis*-tribromide **16**, and *endo-cis*-tribromide **17** were isolated (Scheme 3).

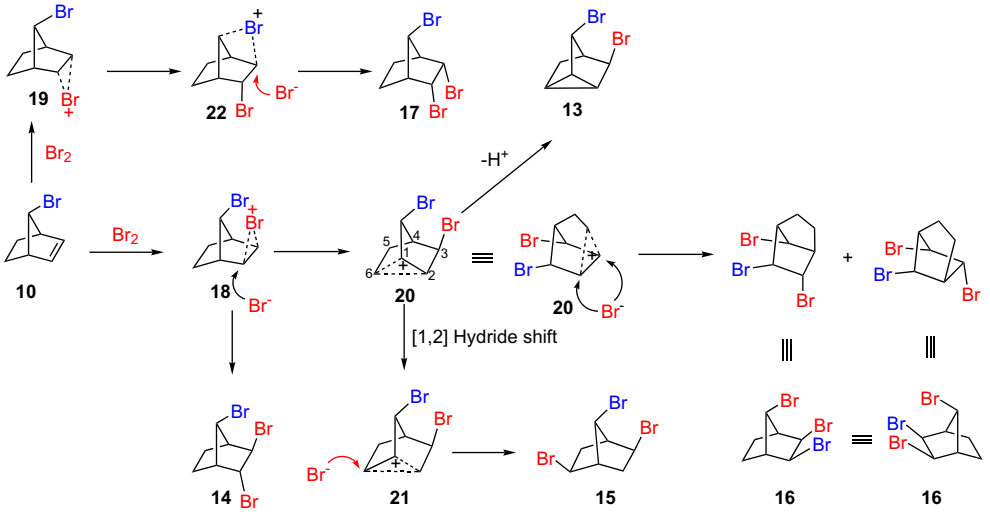
To rationalize the formation of the isomeric bromides **13**–**17** formed at −20 °C we propose the following mechanism (Scheme 4).

Electrophilic bromine can attack the double bond in **10** from both *endo* and *exo*-face of the double bond to form the cyclic bromonium ions **18** and **19**, respectively (Scheme 4). It is evident from the configuration of the bromine atoms in **15** and **16** that the initial attack by bromine has occurred from the *exo*-face of the double bond. The formed bromonium ion **18** can rearrange to the non-classical carbocation **20**. The symmetrical non-classical carbocation **20** can be trapped by the bromide ion to give the cis-product **16**.

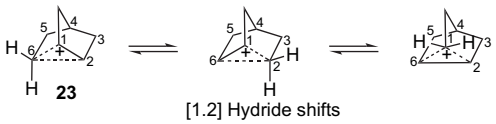
It is expected that the carbon atoms C-1 and C-2 in the unsubstituted norbornyl cation **23** to be equivalent whether the carbocation is classical or non-classical (Scheme 5). However, the NMR spectral measurement carried out at −70 °C shows also their equivalence with the carbon atom C-6. This can be explained by rapid 1,2,6-hydride shifts between these three carbon atoms that interconverts these positions.[46–48] Therefore, the symmetrical intermediate **20** would follow the same way and generate the non-classical carbocation **21** by [1,2]-hydride shift. The bromide anion can attack the carbon atom C-6 in **21** from the backside and form the rearranged tribromide **15**. The formation of **14** is straightforward. It is likely that this compound has been formed by the trans-opening of the formed intermediates such as **18** or **19**. The unusual stereochemistry of the bromine atoms in **17** can be understood from neighboring group participation. Backside attack of bromine bonded to the bridgehead carbon atom (C-7) in **19** on carbon atom involved in the three-membered bromonium ion



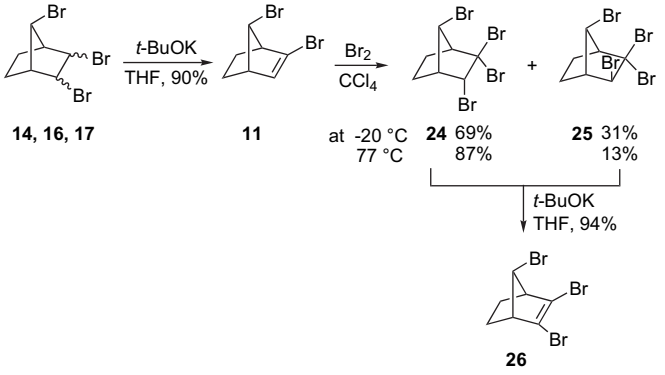
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

can form the four-membered ring bromonium ion **22**. A second backside attack on carbon atom C-3 can form the cis-addition product **17**. The cyclopropanoid compound **13** can easily formed by proton-elimination from the intermediate **20**. The dibromide **13** could be the source for the formation of **14**, **15** or **16** by a ring-opening reaction with HBr. It was noticed that **13** was stable when treated with HBr under the given reaction conditions.

The high temperature bromination of **10** gave mainly three non-rearranged products **14**, **16**, and **17** in 75, 8, and 17% yields, respectively. The mechanism of bromine addition at high temperatures is different than the mechanism at low temperatures. We demonstrated that at high temperatures bromine radicals are involved.[31–35] Since the radicals have a very low tendency for rearrangement, mostly non-rearranged products are formed during reactions done at high temperatures.

After the completion of the bromination reaction of **10** at different temperatures, we focused on the bromination reaction of **11** to investigate the effect of bromine atoms on the tendency of skeletal rearrangement. Elimination of tribromides **14/16/17**, which was obtained by the bromination of monobromide **10**, gave the starting material, dibromide **11** in 90% yield (Scheme 6). The bromination of **11** at −20 °C resulted in the formation of only non-rearranged products **24** (69%) and **25** (31%). On the other hand, high temperature bromination of **11** gave also the same products (**24** and **25**) in 87 and 13% yields, respectively. HBr elimination from tetrabromides **24** and **25** with potassium *tert*-butoxide at room temperature gave tribromide **26** in high yield (Scheme 6).

Comparison of the low temperature bromination reactions of **10** and **11** shows that the introduction of an additional bromine atom to the double bond (**11**) changes the amount of the non-rearranged products from 25–40% (in the case of **10**) up to 100% (in the case of **11**). The position and number of the bromine atoms play an important role in determination of the mode of the bromination reaction. A bromine atom attached to the double bond and bridge carbon atom as in the case of **11** completely prevents the skeletal rearrangement in the norbornene system.

2.1. NMR spectral studies and configurational assignments

The structures of these compounds have been elucidated on the basis of ^{1}H and ^{13}C NMR spectral data (APT, HETCOR, and COSY) and extensive double resonance experiments and by comparison of some spectral data of related systems reported in the literature.[24–30,41] We mainly used the coupling constants between the relevant protons to assign the correct configuration of the bromine atoms. The high value of J_{12}, J_{34}, J_{45}, and J_{61} (3.3–4.0 Hz) is uniquely accommodated by the *exo*-orientation of the protons (*endo*-orientation of bromine atoms) at C_2, C_3, C_5, and C_6 carbon atoms. On the other hand, the absence of any coupling between the related protons confirms the *endo*-orientation of protons at C_2, C_3, C_5, and C_6,

which in turn proves the *exo*-orientation of the bromine atoms. In the rigid systems, if the bonding arrangement of the protons meets **W** or **M** criterion as shown below (Fig. 2), long-range coupling constants of value of J=0.9–1.3 Hz are observed. The observed coupling constant between the bridge proton and the other protons reveal the exact position of the substituents.

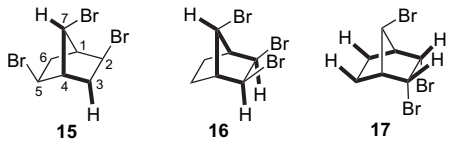
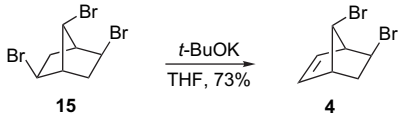


Figure 2.

The tribromides **16**, **17**, and **26** could be characterized easily because of the symmetrical structures, exhibiting four-line ^{13}C NMR spectra. To determine the position of the bromine atoms in **15**, tribromide was treated with 1 equiv of potassium *tert*-butoxide, which produced the known compound **4** (Scheme 7).[30] This reaction indicates the position of three bromine atoms in the original molecule.



Scheme 7.

2.2. γ-gauche Effect

It is well known that interactions related to the van der Waals effect cause a paramagnetic contribution to the shielding constants, which results in shifts of the proton resonances to lower field and the resonances of the directly connected carbon atoms to higher field.[49–52] The γ-*gauche* effects are better observed in conformationally rigid systems and it can be applied to the configurational assignments of the molecules.[53,54] For example, in the molecules **14**, **16**, and **17**, γ-*gauche* effect can be observed depending on the configuration of the bromine atoms (Fig. 3). Comparison of the bridge carbon resonances reveal that the *exo*-orientation of one of the bromine atom in **14** causes an upfield shift of the bridge carbon resonance about 2.1 ppm, and the second *exo*-bromine in **16** causes an additional upfield shift of 1.7 ppm. Similar effects are also observed in the resonances of the methylenic protons as well as the corresponding carbon atoms.

The methylene protons of norbornane resonate at 1.21 ppm. The methylene proton resonances (H-5$_{endo}$ and H-6$_{endo}$) in **16** resonate at 1.38 ppm. This value is comparable with those of unsubstituted norbornane. The *endo*-orientation of two bromine atoms in **17** causes a remarkable lowfield shift (2.12 ppm) due to the steric repulsion caused by bromine atoms. In the case of **14**, there is a remarkable chemical shift

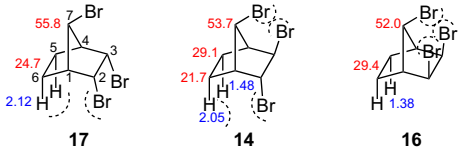


Figure 3.

difference between the *endo*-methylenic protons. The proton H-5$_{endo}$ resonates at 1.48 ppm whereas the proton H-6$_{endo}$ appears at lower field (2.05 ppm). Similar chemical shift differences are also observed in the carbon resonances of C-5 and C-6. A chemical shift difference of about 7.4 ppm in the resonances of the corresponding carbon atoms is also remarkable and helpful by the assignment of the correct configuration of those molecules.

3. Experimental

3.1. General

Melting points were determined on a Büchi model 530 apparatus and are uncorrected. Infrared spectra were recorded on a Mattson model 1000 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on 200 (50) and 400 (100) MHz spectrometers. Mass spectra (EI) were recorded at 70 eV as *m*/*z*. All solvents were dried and distilled before use. Column chromatography was performed on silica gel 60 (70–230 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. All substances reported in this paper, are in their racemic form.

Caution. It has been reported[30] that of three laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders, which contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. In the case of bromides derived from norbornene there is no report in the literature about the toxicological effect. However, we recommend that the compounds must be handled only with extreme caution.

3.2. 1R(S),2S(R),4S(R),7R(S)-2,7-Dibromobicyclo[2.2.1]-heptane (*12*)

The rearranged dibromide **12** was prepared in 41% yield as described in the literature.[23,41] Pale yellow liquid; δ_H (200 MHz, $CDCl_3$) 3.96 (m, 2H, H_2 and H_7), 2.67 (m, 2H, H_1 and H_4), 2.44 (m, 1H, H_{3exo}), 2.25 (dd, $J_{3,3'}$=13.5 Hz, $J_{3endo,2endo}$=8.6 Hz, 1H, H_{3endo}), 1.77–1.64 (m, 2H, H_6), 1.40–1.23 (m, 2H, H_5); δ_C (50 MHz, $CDCl_3$) 55.6, 52.4, 50.0, 46.5, 44.0, 30.4, 27.2.

3.3. Synthesis of syn-1R(S),4S(R))-7-bromobicyclo[2.2.1]-hept-2-ene (*10*)

To a stirred solution of dibromide **12** (1.00 g, 3.94 mmol) in 30 mL of dry and freshly distilled THF was added potassium *tert*-butoxide (1.76 g, 15.71 mmol). The reaction mixture was

stirred at room temperature for 48 h. After removal of the solvent, the mixture was diluted with water (20 mL) and the aqueous solution was extracted with ether (3×50 mL). The combined organic layers were washed with water (2×30 mL), dried over $CaCl_2$, and concentrated. The residue was filtered through a short silica gel column (10 g) eluting with hexane to give 600 mg (88%) of **10**.[41] Colorless liquid; R_f (*n*-hexane) 0.73; δ_H (200 MHz, $CDCl_3$) 6.01 (m, 2H, H_2 and H_3), 3.86 (m, 1H, H_7), 3.02 (m, 2H, H_1 and H_4), 1.77 (AA′ part of AA′BB′ system, 2H, H_{5exo} and H_{6exo}), 1.10 (BB′ part of AA′BB′ system, 2H, H_{5endo} and H_{6endo}); δ_C (50 MHz, $CDCl_3$) 134.9 (C_2 and C_3), 68.1 (C_7), 51.4 (C_1 and C_4), 24.7 (C_5 and C_6); ν_{max} (KBr) 3068, 2979, 2875, 1466, 1343, 1297, 1235, 1123, 931 cm^{-1}; MS (EI) *m/z* 174/172 (M^+, 48), 146/144 ($M^+-C_2H_4$, 100), 93/91 (M^+−Br, 93), 65 (84).

3.4. Bromination of monobromide 10 at −20 °C

To a stirred solution of bromide **10** (1.00 g, 5.78 mmol) in 30 mL of carbon tetrachloride cooled to −20 °C was added dropwise a cooled solution of bromine (1.11 g, 6.94 mmol) in 10 mL of carbon tetrachloride over a period of 10 min. After stirring for 30 min at −20 °C, the solution was allowed to come to room temperature. The solvent was evaporated and the oily residue was chromatographed on silica gel (100 g) eluting with hexane. Five products were isolated in the following order: **17** (77 mg, 4%), **14** (422 mg, 22%), **16** (345 mg, 18%), **15** (365 mg, 19%), **13** (536 mg, 37%).

3.4.1. syn-1R(S),2R(S),3S(R),4S(R)-2,3,7-Tribromobicyclo-[2.2.1]heptane (17)

White solid; mp 93−94 °C from ether/hexane (1:3); R_f (*n*-hexane) 0.40; δ_H (200 MHz, $CDCl_3$) 4.98 (AA′ part of AA′XX′ system, 2H, H_2 and H_3), 4.25 (t, $J_{1,7}=J_{4,7}=1.8$ Hz, 1H, H_7), 2.55 (XX′ part of AA′XX′ system, 2H, H_1 and H_4), 2.12 (AA′ part of AA′BB′ system, 2H, H_{5endo} and H_{6endo}), 1.64 (BB′ part of AA′BB′ system, 2H, H_{5exo} and H_{6exo}); δ_C (50 MHz, $CDCl_3$) 56.1 (C_2 and C_3), 55.8 (C_7), 51.6 (C_1 and C_4), 24.7 (C_5 and C_6); ν_{max} (KBr) 2923, 1457, 1396, 1319, 1226, 1002, 910, 802, 740 cm^{-1}; MS (EI) *m/z* 336/334/332/330 (M^+, 8), 255/253/251 (M^+−Br, 80), 173/171 (M^+−2Br, 44), 92/91 (M^+−3Br, 100), 65 (38). Anal. Calcd for $C_7H_9Br_3$: C, 25.26; H, 2.73. Found: C, 25.58; H, 3.02.

3.4.2. syn-1R(S),2R(S),3R(S),4S(R)-2,3,7-Tribromobicyclo-[2.2.1]heptane (14)

Colorless liquid; R_f (*n*-hexane) 0.33; δ_H (400 MHz, $CDCl_3$) 5.05 (ddd, $J_{2,3}=4.8$ Hz, $J_{1,2}=4.0$ Hz, $J_{2,6exo}=2.0$ Hz, 1H, H_2), 4.07 (dt, $J_{3,7}=2.2$ Hz, $J_{1,7}=J_{4,7}=1.7$ Hz, 1H, H_7), 3.86 (dd, $J_{2,3}=4.8$ Hz, $J_{3,7}=2.2$ Hz, 1H, H_3), 2.66 (br d, $J_{4,5exo}=4.4$ Hz, 1H, H_4), 2.60 (ddd, $J_{1,6exo}=4.6$ Hz, $J_{1,2}=4.0$ Hz, $J_{1,7}=1.7$ Hz, 1H, H_1), 2.05 (ddd, A part of AB system, $J_{6endo,6exo}=13.0$ Hz, $J_{6endo,\ 5endo}=9.9$ Hz, $J_{6endo,5exo}=4.6$ Hz, 1H, H_{6endo}), 1.79 (dddd, A part of AB system, $J_{5endo,5exo}=12.7$ Hz, $J_{5exo,6exo}=9.0$ Hz, $J_{5exo,6endo}=4.6$ Hz, $J_{4,5exo}=4.4$ Hz, 1H, H_{5exo}), 1.67 (dddt, B part of AB system, $J_{6exo,6endo}=13.0$ Hz, $J_{6exo,5exo}=9.0$ Hz, $J_{6exo,5endo}=J_{6exo,1}=4.6$ Hz, $J_{6exo,2}=2.0$ Hz, 1H, H_{6exo}), 1.48 (ddd, B part of AB system, $J_{5endo,5exo}=12.7$ Hz, $J_{5endo,\ 6endo}=9.9$ Hz, $J_{5endo,\ 6exo}=4.6$ Hz, 1H, H_{5endo}); δ_C (100 MHz, $CDCl_3$) 60.3 (C_2), 56.0 (C_3), 53.7 (C_7), 51.5 (C_4), 51.4 (C_1), 29.1 (C_5), 21.7 (C_6); ν_{max} ($CHCl_3$) 2985, 2962, 2885, 1465, 1303, 1249, 1226, 1195, 1141, 1033, 1010, 979, 941, 887, 809, 771, 732, 632 cm^{-1}; MS (EI) *m/z* 336/334/332/330 (M^+, 5), 255/253/251 (M^+−Br, 92), 173/171 (M^+−2Br, 56), 92/91 (M^+−3Br, 100), 65 (49). Anal. Calcd for $C_7H_9Br_3$: C, 25.26; H, 2.73. Found: C, 25.56; H, 3.07.

3.4.3. syn-1R(S),2S(R),3R(S),4S(R)-2,3,7-Tribromobicyclo-[2.2.1]heptane (16)

Colorless plates; mp 177−178 °C from ether/hexane (1:3); R_f (*n*-hexane) 0.17; δ_H (200 MHz, $CDCl_3$) 4.37 (d, X_2 part of AX_2 system, $J_{2,7}=J_{3,7}=1.3$ Hz, 2H, H_2 and H_3), 3.99 (p, A part of AX_2 system, $J_{2,7}=J_{3,7}=J_{1,7}=J_{4,7}=1.3$ Hz, 1H, H_7), 2.89 (m, 2H, H_1 and H_4), 1.79 (AA′ part of AA′BB′ system, 2H, H_{5exo} and H_{6exo}), 1.38 (BB′ part of AA′BB′ system, 2H, H_{5endo} and H_{6endo}); δ_C (50 MHz, $CDCl_3$) 56.1 (C_2 and C_3), 53.6 (C_1 and C_4), 52.0 (C_7), 29.4 (C_5 and C_6); ν_{max} (KBr) 3023, 2985, 2892, 1519, 1465, 1427, 1303, 1218, 1041, 925, 763, 671, 609 cm^{-1}; MS (EI) *m/z* 336/334/332/330 (M^+, 28), 255/253/251 (M^+−Br, 55), 173/171 (M^+−2Br, 40), 92/91 (M^+−3Br, 100), 65 (40). Anal. Calcd for $C_7H_9Br_3$: C, 25.26; H, 2.73. Found: C, 25.51; H, 2.96.

3.4.4. syn-1R(S),2R(S),4R(S),5S(R)-2,5,7-Tribromobicyclo-[2.2.1]heptane (15)

White solid; mp 57−58 °C from ether/hexane (1:3); R_f (*n*-hexane) 0.10; δ_H (400 MHz, $CDCl_3$) 4.52 (m, 1H, H_7), 3.88 (dd, $J_{5,6endo}=7.5$ Hz, $J_{5,6exo}=5.1$ Hz, 1H, H_5), 3.84 (ddd, $J_{2,3endo}=8.2$ Hz, $J_{2,3exo}=5.1$ Hz, 1H, $J_{2,7}=1.5$ Hz, H_2), 2.78 (m, 1H, H_1), 2.74−2.67 (m, 2H, H_4 and one proton of CH_2), 2.34 (m, 1H, one proton of CH_2), 2.28 (m, 2H, CH_2); δ_C (100 MHz, $CDCl_3$) 54.6, 51.4, 50.6, 46.1, 45.8, 43.1, 40.1; ν_{max} (KBr) 2976, 2936, 2851, 1497, 1441, 1306, 1283, 1250, 1186, 1163, 1134, 1054, 1026, 1000, 974, 936, 913, 894, 880, 865 cm^{-1}; MS (EI) *m/z* 336/334/332/330 (M^+, 5), 255/253/251 (M^+−Br, 79), 173/171 (M^+−2Br, 42), 92/91 (M^+−3Br, 100), 65 (44). Anal. Calcd for $C_7H_9Br_3$: C, 25.26; H, 2.73. Found: C, 25.04; H, 2.95.

3.4.5. 2R(S),3S(R),5R(S),6S(R)-3,5-Dibromotricyclo-[2.2.1.$0^{2,6}$]heptane (13)

White crystals; mp 59−60 °C from chloroform/hexane (1:3); R_f (*n*-hexane) 0.09; δ_H (200 MHz, $CDCl_3$) 4.09 (m, 2H, H_3 and H_5), 2.50 (m, 1H, H_4), 1.92 (dd, B_2 part of AB_2 system, $J_{2,6}=J_{1,6}=5.4$ Hz, $J_{1,5}=J_{2,3}=0.8$ Hz, 2H, H_1 and H_2), 1.45 (m, 2H, H_7), 1.38 (tt, A part of AB_2 system, $J_{2,6}=J_{1,6}=5.4$ Hz, $J_{6,7}=1.2$ Hz, 1H, H_6); δ_C (50 MHz, $CDCl_3$) 53.4, 43.4, 34.0, 22.0, 17.3; ν_{max} (KBr) 3081, 2956, 2876, 1461, 1344, 1311, 1284, 1268, 1254, 1232, 1145, 1066, 1023, 1012, 979, 941, 914, 881, 813, 737, 726, 704 cm^{-1}; MS (EI) *m/z* 254/252/250 (M^+, 22), 173/171 (M^+−Br, 68), 92/91 (M^+−2Br, 100), 65 (25). Anal. Calcd for $C_7H_8Br_2$: C, 33.37; H, 3.20. Found: C, 33.16; H, 3.36.

3.5. Bromination of monobromide **10** at 77 °C

Bromide **10** (1.00 g, 5.78 mmol) was dissolved in 30 mL of carbon tetrachloride in a 100 mL flask, which was equipped with a reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution was added dropwise a hot solution of bromine (1.00 g, 6.25 mmol) in 10 mL of carbon tetrachloride over a period of 10 min. The resulting reaction mixture was heated for 10 min at reflux temperature. After being cooled to room temperature the solvent was evaporated. The oily residue was chromatographed on silica gel (100 g) eluting with hexane. Three products were isolated in the following order: **17** (326 mg, 17%), **14** (1.44 g, 75%), and **16** (154 mg, 8%).

3.6. Synthesis of dibromide (**11**)

To a stirred solution of a mixture of tribromides **14/16/17** (2.50 g, 7.50 mmol) in 40 mL of dry THF was added 1.00 g (8.93 mmol) of potassium *tert*-butoxide. The reaction mixture was stirred overnight at room temperature. After workup as described for **10**, the residue was filtered on a short silica gel column (10 g) eluting with hexane to give 1.80 g (95%) of dibromide **11**.

3.6.1. 1S(R),4S(R),7R(S)-2,7-Dibromobicyclo[2.2.1]-hept-2-ene (**11**)

Colorless liquid; R_f (*n*-hexane) 0.80; δ_H (200 MHz, $CDCl_3$) 6.06 (d, $J_{3,4}$=3.2 Hz, 1H, H_3), 3.84 (m, 1H, H_7), 3.03 (m, 2H, H_1 and H_4), 1.81 (m, 2H, H_{5exo} and H_{6exo}), 1.32 (m, 2H, H_{5endo} and H_{6endo}); δ_C (50 MHz, $CDCl_3$) 133.9, 126.1, 66.1, 59.6, 53.3, 26.2, 24.7; ν_{max} ($CHCl_3$) 2975, 2946, 2910, 2875, 1583, 1461, 1447, 1305, 1281, 1227, 1216, 1190, 1160, 1121, 1031, 974, 961, 939, 921, 868, 825, 803, 778 cm^{-1}; MS (EI) *m/z* 254/252/250 (M^+, 45), 226/224/222 ($M^+-C_2H_4$, 100), 173/171 (M^+−Br, 37), 145/143 ($M^+-C_2H_4$−Br, 90), 92/91 (M^+−2Br, 63), 63 (32). Anal. Calcd for $C_7H_8Br_2$: C, 33.37; H, 3.20. Found: C, 33.56; H, 3.59.

3.7. Bromination of dibromide **11** at −20 °C

The reaction was carried out as described above by using 600 mg (2.38 mmol) of dibromide **11** and 0.46 g (2.88 mmol) of bromine in 20 mL of carbon tetrachloride. The reaction was completed after 8 h. The crude product was chromatographed on silica gel eluting with hexane to give 680 mg (69%) of *endo*-tetrabromide **24** as the first fraction and 300 mg (31%) of *exo*-tetrabromide **25** as the second fraction.

3.7.1. 1S(R),3R(S),4R(S),7R(S)-2,2,3,7-Tetrabromobicyclo-[2.2.1]heptane (**24**)

White solid; mp 85−86 °C from chloroform/hexane (1:3); R_f (*n*-hexane) 0.27; δ_H (400 MHz, $CDCl_3$) 5.59 (dd, $J_{3,4}$=3.3 Hz, $J_{3,5exo}$=1.8 Hz, 1H, H_3), 4.36 (m, 1H, H_7), 3.19 (br d, $J_{1,6exo}$=3.2 Hz, 1H, H_1), 2.51 (m, 1H, H_4), 2.37 (m, 1H, methylenic proton), 1.92−1.63 (m, 3H, methylenic protons); δ_C (50 MHz, $CDCl_3$) 68.9, 68.4, 61.4, 54.0, 51.5, 32.0, 20.7; ν_{max} (KBr) 2977, 2951, 2880, 1466, 1447, 1314, 1289, 1251, 1229, 1215, 1198, 1138, 1011, 986, 941, 913, 818, 767, 734, 638 cm^{-1}; MS (EI) *m/z* 416/414/412/410/408 (M^+, 1), 335/333/331/329 (M^+−Br, 68), 253/251/249 (M^+−2Br, 32), 225/224 ($M^+-2Br-C_2H_4$, 32), 171/169 (M^+−3Br, 100), 92/91 (M^+−4Br, 76), 65 (35). Anal. Calcd for $C_7H_8Br_4$: C, 20.42; H, 1.96. Found: C, 20.32; H, 1.97.

3.7.2. 1S(R),3S(R),4R(S),7R(S)-2,2,3,7-Tetrabromobicyclo-[2.2.1]heptane (**25**)

White solid; mp 186−187 °C from methylene chloride/hexane (1:3); R_f (*n*-hexane) 0.10; δ_H (400 MHz, $CDCl_3$) 4.74 (d, $J_{3,7}$=2.0 Hz, 1H, H_3), 4.18 (m, 1H, H_7), 3.30 (br d, $J_{1,6exo}$=4.0, 1H, H_1), 2.74 (br d, $J_{4,5exo}$=4.8 Hz, 1H, H_4), 2.42 (m, 1H, H_{6endo}), 1.86 (m, 1H, H_{5exo}), 1.80 (m, 1H, H_{6exo}), 1.52 (m, 1H, H_{5endo}); δ_C (100 MHz, $CDCl_3$) 70.0, 66.3, 60.5, 53,2, 48.4, 28.2, 27.5; ν_{max} (KBr) 2989, 2945, 2879, 1462, 1445, 1303, 1264, 1231, 1209, 1193, 1171, 1144, 1006, 982, 938, 902, 812, 773, 751, 729, 644, 606 cm^{-1}; MS (EI) *m/z* 416/414/412/410/408 (M^+, 2), 335/333/331/329 (M^+−Br, 74), 253/251/249 (M^+−2Br, 40), 225/224 ($M^+-2Br-C_2H_4$, 30), 171/169 (M^+−3Br, 100), 92/91 (M^+−4Br, 63), 65 (34). Anal. Calcd for $C_7H_8Br_4$: C, 20.42; H, 1.96. Found: C, 20.43; H, 2.03.

3.8. Bromination of dibromide **11** at 77 °C

The reaction was carried out as described for **10** by using 600 mg (2.38 mmol) of dibromide **11** and 0.46 g (2.88 mmol) of bromine. After chromatographic separation (silica gel, hexane) 850 mg (87%) of **24** and 130 mg (13%) of **25** were obtained.

3.9. Reaction of tetrabromides **24** and **25** with potassium *tert*-butoxide

The reaction was carried out as described for **10** by using 1.00 g (2.43 mmol) of a mixture of **24** and **25** and 1.09 g (9.73 mmol) of potassium *tert*-butoxide. The crude product was crystallized from ether/hexane (1:3) to give 750 mg (94%) of tribromo norbornene **26**.

3.9.1. syn-(1R(S),4S(R))-2,3,7-Tribromobicyclo[2.2.1]-hept-2-ene (**26**)

Colorless needles; mp 74−75 °C; δ_H (200 MHz, $CDCl_3$) 3.88 (t, $J_{1,7}=J_{4,7}$=1.8 Hz, 1H, H_7), 3.14 (m, 2H, H_1 and H_4), 1.84 (AA′ part of AA′BB′ system, 2H, H_{5exo} and H_{6exo}), 1.47 (BB′ part of AA′BB′ system, 2H, H_{5endo} and H_{6endo}); δ_C (50 MHz, $CDCl_3$) 125.7 (C_2 and C_3), 63.7 (C_7), 60.4 (C_1 and C_4), 26.1 (C_5 and C_6); ν_{max} (KBr) 2970, 2942, 2904, 2866, 1591, 1457, 1444, 1297, 1226, 1160, 1122, 1090, 1041, 956, 932, 907, 866, 820, 806 cm^{-1}; MS (EI) *m/z* 334/332/330/328 (M^+, 37), 306/304/302/300 ($M^+-C_2H_4$, 82), 225/223/221 ($M^+-C_2H_4$−Br, 100), 171/169 (M^+−2Br, 31), 91 (M^+−3Br, 43), 63 (36). Anal. Calcd for $C_7H_7Br_3$: C, 25.41; H, 2.13. Found: C, 25.26; H, 2.20.

3.10. Reaction of tribromide **15** with potassium tert-butoxide

To a stirred solution of tribromide **15** (200 mg, 0.60 mmol) in 15 mL of dry THF was added 80 mg (0.71 mmol) of potassium *tert*-butoxide. The reaction mixture was stirred overnight at room temperature. After workup as described for **10**, the residue was filtered on a short silica gel column (10 g) eluting with hexane to give 110 mg (73%) of dibromide **4**.[30]

3.10.1. 1R(S),4R(S),5S(R),7R(S)-5,7-Dibromobicyclo-[2.2.1]hept-2-ene (**4**)

Pale yellow liquid; R_f (*n*-hexane) 0.23; δ_H (200 MHz, $CDCl_3$); 6.18 (m, 2H, H_2 and H_3), 4.08 (m, 1H, H_7), 3.76 (ddd, $J_{5,6endo}$=7.9 Hz, $J_{5,6exo}$=4.0 Hz, $J_{5,7}$=1.5 Hz, 1H, H_5), 3.21 (m, 1H, H_4), 3.00 (m, 1H, H_1), 2.63 (dt, A part of AB system, $J_{6,6'}$=13.2 Hz, $J_{5,6exo}$=$J_{1,6exo}$=4.0 Hz, 1H, H_{6exo}), 2.05 (ddd, B part of AB system, $J_{6,6'}$=13.2 Hz, $J_{5,6endo}$=7.9 Hz, $J_{6endo,7}$=0.8 Hz, 1H, H_{6endo}); δ_C (50 MHz, $CDCl_3$) 140.0, 137.9, 58.5, 56.3, 50.9, 46.1, 35.3; ν_{max} ($CHCl_3$) 2990, 2920, 2850, 1495, 1460, 1440, 1376, 1316, 1296, 1269, 1249, 1219, 1152, 1129, 1018, 1005, 983, 896, 859, 791, 752, 709 cm^{-1}; MS (EI) *m/z* 254/252/250 (M^+, 11), 173/171 (M^+-Br, 100), 146/144 ($M^+-Br-C_2H_3$, 63), 92/91 (M^+-2Br, 91), 65 (75).

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