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High Temperature Bromination. Part 12:[1] Bromination of 7-Oxabenzonorbornadiene: Synthesis of 2,3-Dibromo-7-oxabenzonorbornadiene

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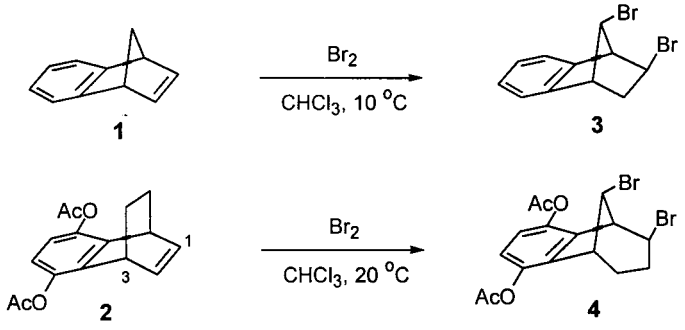
Abstract—The electrophilic addition of bromine to 7-oxabenzonorbornadiene (**8**) at 0°C led in high yield to the formation of dibromoaldehyde **10**. However, high-temperature bromination of **8** in carbon tetrachloride at 77°C gave non-rearranged products **17** and **18**. From the elimination of non-rearranged products, 2-bromo-7-oxabenzonorbornadiene (**12**) was obtained. Similarly, bromination of monobromide **12** at 77°C yielded the non-rearranged tribromides **19** and **20** while bromination of 12 at 0°C gave the rearranged product **11**. The dehydrobromination of tribromides (**19**, **20**) provided the 2,3-dibromo-7-oxabenzonorbornadiene (**21**), which is a synthon for the trimerization, in high yield

Introduction

The addition of bromine to the carbon–carbon double bond is formally one of the simplest reactions typical of unsaturated compounds.[2] The nature of the intermediates of the addition depends on the structure of the substrate and on the reaction medium. The intermediates, strongly bridged bromonium ions, are involved in the bromination of nonconjugated olefines that give *anti*-adducts. However, bromination of unsaturated bicyclic systems leads to rearrangements of the molecular skeleton. For example, the electrophilic addition of bromine to benzonorbornadiene (**1**)[3] and 5,8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalane (**2**)[4] leads to the formation of rearranged products **3** and **4** almost in quantitative yield (Scheme 1). Recently, Smith[5] has proposed that the stereochemistry in **4** is best accommodated by a synchronous concerted electrophilic addition of bromine across carbons **1** and **3**, and that it proceeds via an ion pair transition structure in which the Wagner–Meerwein portion of the reaction has already occurred. These results were calculated at the Becke3LYP/6-31G* level.

However, the reaction temperature has a dramatic influence on the product distribution.[6] High temperature bromination of **1**[7] at 150°C results in the formation of non-rearranged products **5**, **6**, **7** and the rearranged product **3** in a ratio of 4:1



Scheme 1.

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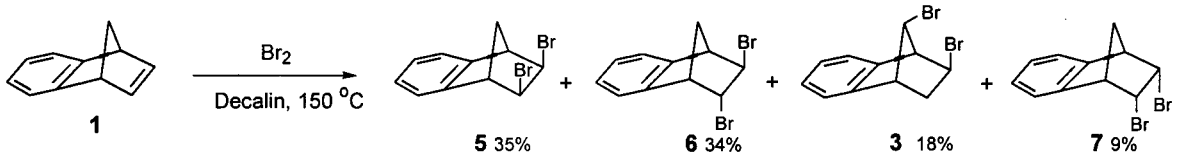
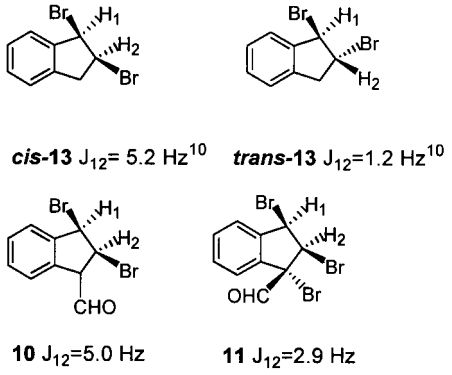


Scheme 2.

(Scheme 2). Conducting the bromination reaction in the presence of free radical inhibitors suppressed the formation of the non-rearranged products. This strongly supports the assumption that there is a competition between the radical and ionic mechanisms and that high temperature bromination is occurring by a free radical mechanism. Since radical intermediates are much less likely to rearrange, at higher temperature we obtained mostly non-rearranged products.

In order to test the behaviour of a oxygen bridging in the bicyclic systems on the product distribution at low- and high-temperature bromination we have investigated the bromination reaction of the 7-oxabenzo-norbornadiene **8** at 0°C and higher temperatures. Furthermore, we were interested in the synthesis of the dibromo-oxabenzonorbornadiene **21** in connection with our trimerization reactions.[8]



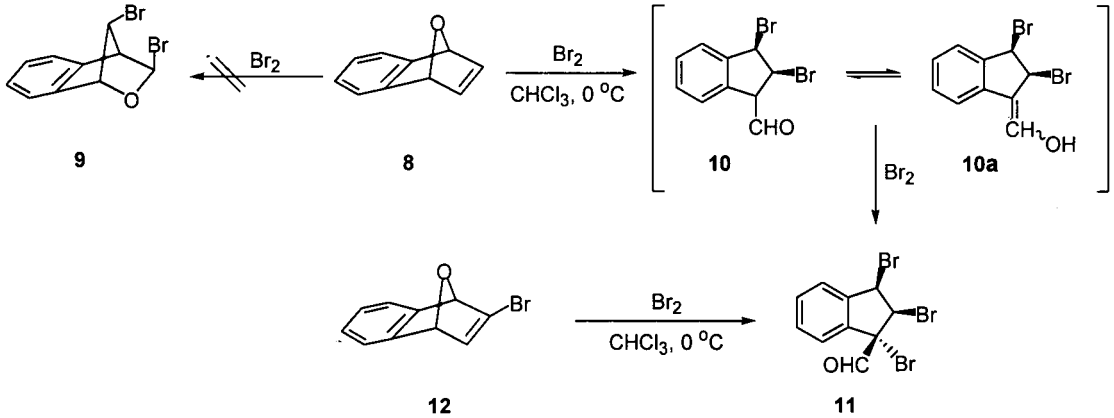
Results and Discussions

Firstly, 7-oxabenzonorbornadiene **8**,[9] synthesized by the addition of benzyne to furan was treated in chloroform with bromine at 0°C. Dibromo aldehyde **10** was formed as the sole product, which was not stable at room temperature (Scheme 3).

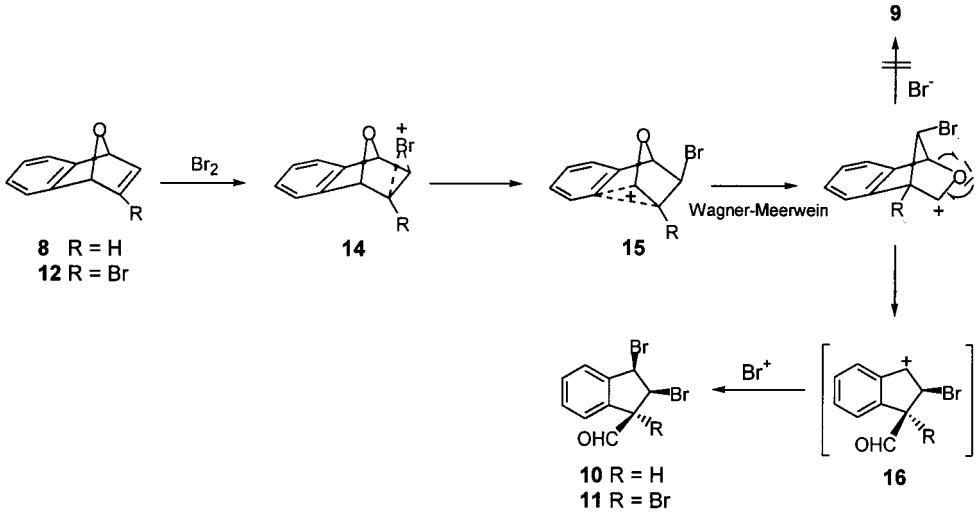
Extensive NMR studies did not reveal the formation of the possible rearranged product **9**. NMR measurements also indicated that this aldehyde is in equilibrium with the corresponding enol **10a**. The configuration of the bromines at the C_2 and C_3 carbons was established by analysis of the AB system arising from the H_2 and H_3 protons. The measured coupling constant J_{23}=5.0 Hz indicates the *cis*-arrangement of the bromine atoms. Comparison of this value with those reported for the *cis*- and *trans*-dibromo-indanes **13** clearly supports the suggested configuration.[10] The H_3 proton resonates at 5.69 ppm as a singlet.

Further bromination of the labile compound **10** with excess bromine gave the stable tribromide **11**, the configuration of which was determined again by ^{1}H NMR spectroscopy. Furthermore, tribromide **11** was synthesized by an independent route from bromo-oxabenzonorbornene **12**. The bromination of **12** at room temperature in chloroform at 0°C provided the same tribromide in a yield of 71%.

For the formation of the rearranged products **10** and **11** we propose the following mechanism. Since the bromine attacks benzonorbornadiene (**1**) exclusively from the *exo*-face of the double bond,[11] we assume that in the case of the bromo-oxabenzonorbornadiene **12**, bromine also attacks the double bond from the exo face to generate *exo*-bromonium cation **14**. Most reasonably, the driving force of this mode of addition is supplied by the formation of aryl bridged intermediate **15**. The formed intermediate can easily rearrange into aldehyde **16** having benzyl cation structure which will be trapped by the attack of bromide ion to form **10**. From the



Scheme 3.



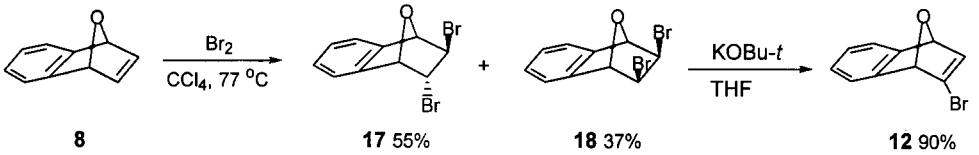
Scheme 4.

bromination reaction mechanism of the 2-bromo-oxobenzonorbornadiene we predict the configuration of the aldehyde group and bromine atom attached at the C_2 carbon atom to have *cis*-configuration (Scheme 4).

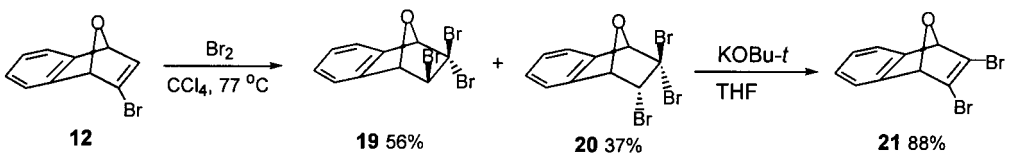
Furthermore, we studied high temperature bromination of 7-oxabenzonorbornadiene (**8**) at 77°C. For this purpose, hot bromine solution in CCl_4 was added directly to refluxing solution of **8** in CCl_4 at 77°C. NMR analysis of the crude product indicated that the reaction mixture consisted of two products. After repeated column chromatography combined with fractional crystallization, we have been able to separate two isomeric compounds **17** and **18** (Scheme 5).

The structures of the products have been elucidated on the basis of ^1H and ^{13}C NMR data and chemical transformations. ^1H NMR spectra of the *cis* isomer **18** reveals sufficient information for tentative assignments to be made. Compound **18** exhibits a AA′BB′ and AA′XX′ coupling pattern arising from the aromatic, bridgehead, and CHBr protons which indicate clearly the symmetrical structure and *syn* addition of bromine. The *exo* stereochemical assignment for the bromine atoms is supported by the absence of a measurable coupling between CHBr protons and bridgehead protons. AM1 calculations support this finding (Dihedral angle between H1 and H10 (H8 and H9) is 89.5°). However, in the case of the trans isomer **17**, there are two different dihedral angles of 89.9 and 38.4°. Therefore, one of the CHBr protons resonates as a doublet while the other proton (H9) resonates as a doublet of doublets due to the coupling with the bridgehead proton H8. ^{13}C NMR spectra of **17** and **18** are completely in agreement with the proposed structures. Treatment of dibromides **17** and **18** with potassium *t*-butoxide gave the monobromide **12** as the sole product in 90% yield (Scheme 6).

Further bromination of the monobromide **12** at 77°C led in high yield to the formation of the non-rearranged products **19** and **20** in high yield. The structures of **19** and **20** have been elucidated on the basis of the spectral data obtained by ^1H NMR and ^{13}C NMR experiments. The configurational assignments of the bromine atoms have been made on the basis of the measured coupling constants between bridgehead proton and CHBr proton. In the case of **20** we extracted a coupling of 4.8 Hz while the other isomer **19** did not show any measurable coupling. Base supported elimination of HBr from **19** and **20** provided the expected dibromo-oxanorbornadiene **21**, which is an important synthon for the trimerization reactions, in 88% yield.



Scheme 5.



Scheme 6.

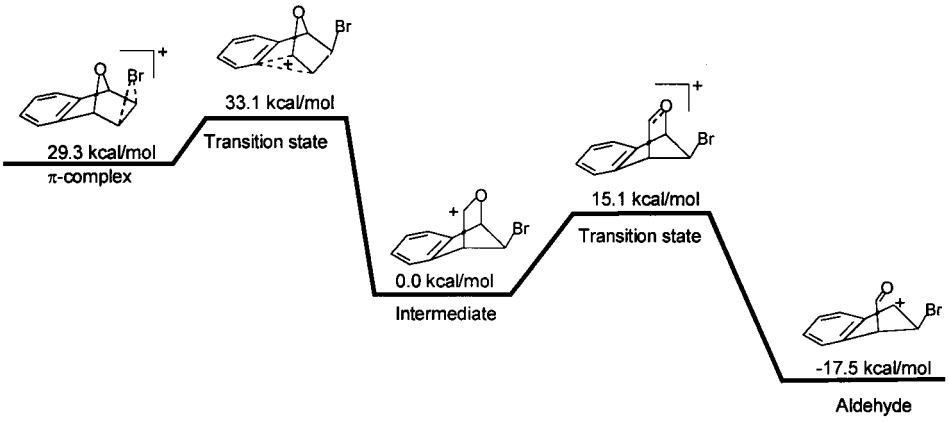


Figure 1. Potential energy diagram (kcal/mol) calculated at the MNDO/d level for the rearrangement of 7-oxabenzonorbornadiene to the aldehyde.

Table 1. Relative energies (kcal/mol) at the MNDO/d level for rearrangement within the brominated (Br cation or Br radical) complexes

	π-Complex	TS	σ-Complex	TS	Intermediate	TS	Aldehyde
7-oxabenzonorbornadine/Br^+	29.3	33.1	[a]		0.0	15.1	−17.5
7-oxabenzonorbornadine/Br·	[a]		−10.7	7.0	0.0		

[a] This species does not exist on the MNDO/d potential energy surface.

In order to shed light on the mechanism of the product formation caused by bromination of **8** at different temperatures we have undertaken some semiemprical calculations at the MNDO/d level to support the experimental results. We used the Hyperchem Molecular Modeling Software, which is quite useful for calculating geometries and relative energies.[12] All minima and transition states were fully optimized and characterized by computing vibrational frequencies (0 imaginary frequencies for minima and 1 imaginary frequency for transition states). The calculations refer to the gas phase while bromination takes place in solution. In the gas phase, the Br–Br bond in molecular bromine is too strong to allow facile complex formation. In solution, where the Br–Br bond is more polarizable, the brominating agent may be Br^+–Br^- or even Br^+. Therefore, the gas phase bromination was modelled with Br^+ as the brominating agent. Our calculations indicate that the initially formed π-complex **14** rearranges with a low barrier into the intermediate **22** through the σ-complex which is, in this case, a transition state. This intermediate rearranges to the more stable aldehyde **16** which will be subsequently captured by bromide to form the corresponding addition products **10** and **11** (Fig. 1 and Table 1). We also considered the free radical brominating agent, Br·. We initially searched for a π complex. However, in the case of Br radical as the brominating agent, the π complex collapsed to a σ complex without barrier, which is completely in agreement with our experimental finding. The addition of a Br radical to **8** has a 17.7 kcal/mol barrier. In contrast, the barrier to addition of Br cation to **8** has a much smaller barrier of 3.8 kcal/mol.

Conclusion

The results of the present work demonstrate that the high temperature bromination is a useful synthetic method to generate the non-rearranged bromine addition products in the unsaturated bicyclic systems, which have a great tendency to undergo Wagner–Meerwein rearrangement. With this methodology we have shown that the application of high temperature bromination to the oxa-benzonorbornadiene **8** provides an important synthetic tool for entry into the substituted oxa-benzonorbornadiene system. Furthermore, we have observed that the tendency of the oxa-benzonorbornadiene system to undergo Wagner–Meerwein rearrangement is less then found in the benzonorbornadiene system. In the case of benzonorbornadiene, a much higher temperature (150°C) was applied to prevent the skeletal rearrangement. Even at this high temperature, ca. 20% of the rearranged products were formed. However, for the oxa-benzonorbornadiene system, a temperature of 77°C was sufficient to prevent skeletal rearrangement. At this temperature, no trace of the rearranged products was detected. We assume that the inductive effect of the bridging oxygen plays an important role in this case. Probably, the tendency of the system to form the bridged nonclassical carbocation **15** is retarded by the oxygen atom.

Experimental

General

Melting points are uncorrected. Infrared spectra were obtained from KBr pellets on a regular instrument. The ^1H and ^{13}C NMR spectra were recorded on 200 (50) MHz spectrometers. Apparent splittings are given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminium plates.

Caution: it has been reported[13] that of the three laboratory workers who have used dibromides and 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 dibromide derived from benzonorbornadiene there is no report in the literature about the toxicological effect. However, we recommend that the compounds must be handled only with extreme caution.

Bromination of 11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (8) with 1 equiv. bromine at 0°C

A solution of **8** (100 mg, 0.69 mmol) in 0.5 mL of CCl_4 was placed into NMR tube and cooled to 0°C. Bromine (113 mg, 0.70 mmol) was added to the solution. The ^{1}H NMR spectrum was recorded immediately. Due to fact that dibromide **10** was unstable, ^{13}C NMR could not be detected.

(1*R*(*S*),2*S*(*R*),3*R*(*S*))-2,3-Dibromo-2,3-dihydro-1*H*-indene-1-carbaldehyde (10/10a). ^{1}H NMR (200 MHz, $CDCl_3$) δ 9,63 (m, OH, 1H), 7.65–7.37 (m, aromatic, 4H), 5.69 (m, H_1, 1H), 5.11 (d, J_{23}=5.0 Hz, H_3, 1H), 4.57 (d, J_{23}=5.0 Hz, H_2, 1H).

Bromination of 11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (8) with 2 equiv. bromine at 0°C

To a magnetically stirred solution of **8** (200 mg, 1.39 mmol) in 5 mL dry chloroform cooled to 0°C was added dropwise a solution of bromine (445 mg, 2.78 mmol) in 2 mL chloroform. The resulting solution was stirred for 30 min. The solvent was evaporated to half the volume and diethyl ether (5 mL) was added to the solution. After standing in a freezer (ca. −20°C) overnight, 367 mg (69%) of the tribromide was crystallized.

(1*S*(*R*),2*R*(*S*),3*R*(*S*))-1,2,3-Tribromo-2,3-dihydro-1*H*-indene-1-carbaldehyde (11). Colourless crystals, mp:135–136°C. [Found: C, 31.21; H, 1.80. $C_{10}H_7Br_3O$ requires C, 31.37; H, 1.84 %]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.52 (s, aldehyde, 1H), 7.71–7.46 (m, aromatic, 4H), 5.66 (d, J_{23}=2.9 Hz, H_3, 1H), 5.15 (d, H_2, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 187.57, 143.08, 138.91, 133.44, 132.61, 129.69, 128.22, 70.07, 59.84, 54.00. IR (KBr, cm^{-1}) 3081, 3055, 3030, 3004, 2979, 2953, 1728, 1472, 1191, 1013, 961, 885, 757.

Bromination of 11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (8) at 77°C

2.0 g (13.89 mmol) of 7-oxabenzonorbornadiene **8** was dissolved in 50 mL of carbon tetrachloride in a 100 mL flask, which was equipped with 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 (2.29 g, 14.31 mmol) in 3 mL of carbon tetrachloride during 5 min. The resulting reaction mixture was heated for 2 min at reflux temperature. After being cooled to room temperature the solvent was evaporated. The residue was chromatographed on silica gel (100 g) eluting with hexane/ethyl acetate in ratio 10:1. The first fraction consisted of the trans dibromide **17**, which was crystallised from methylene chloride/hexane (1/2).

(1*R*(*S*),8*S*(*R*),9*S*(*R*),10*S*(*R*))-9,10-Dibromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (17). 2.32 g (55%), Colourless crystals, mp: 91–92°C. [Found: C, 39.19; H, 2.51. $C_{10}H_8Br_2O$ requires C, 39.51; H, 2.65%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43–7.28 (m, aromatic, 4H), 5.46 (bs, H_1, 1H), 5.44 (d, J_{89}=4.6 Hz, H_8, 1H), 4.54 (dd, J_{89}=4.6 and J_{910}=2.6 Hz, H_9, 1H), 3.82 (d, J_{910}=2.6, H_{10}, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.61, 143.46, 130.24, 129.67, 125.31, 121.91, 89.12, 85.11, 55.24, 52.80. IR (KBr, cm^{-1}) 3080, 3055, 3029, 3004, 2979, 1472, 1242, 1217, 1191, 1165, 987. The second fraction consisted of the *exo-cis* dibromide **18** that was crystallised from methylene chloride/hexane (1/2).

(1*R*(*S*),8*S*(*R*),9*S*(*R*),10*R*(*S*))-9,10-Dibromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (18). 1.56 g (37%). Colourless crystals, mp: 146–147°C. [Found: C, 39.42; H, 2.75. $C_{10}H_8Br_2O$ requires C, 39.51; H, 2.65 %]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36–7.24 (AA′BB′ system, aromatic, 4H), 5.49 (bs, H_1, H_8, 2H), 4.22 (bs, H_9, H_{10}, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.68, 130.42, 122.48, 89.76, 54.08. IR (KBr, cm^{-1}) 3106, 3029, 3004, 1472, 1217, 1191, 1165, 1012, 987, 859, 782.

Elimination of dibromide 17

To a stirred solution of dibromide **17** (2.0 g, 6.58 mmol) in dry and freshly distilled THF (20 mL) was added 811 mg (7.2 mmol) of potassium *tert*-butoxide solution in THF (10 mL). The resulting reaction mixture was heated for 3 h at reflux temperature. After being cooled to room temperature the solvent was evaporated. The mixture was diluted with water and the aqueous solution was extracted with ether (3×50 mL), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was filtered on a short silica gel column (10 g) eluted with hexane/ethyl acetate (10:1) to give 1.32 g (90%) of monobromide **12** as the sole product. From the elimination of **18** under the same reaction condition, monobromide **12** was obtained as the sole product in 90% yield.

(1*S*(*R*),8*S*(*R*))-9-Bromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (12). Colourless crystals from methylene chloride/hexane 1/3, mp: 45–46°C. [Found: C, 53.52; H, 3.32. $C_{10}H_7BrO$ requires C, 53.84; H, 3.16%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.42–7.00 (m, aromatic, 4H), 6.96 (d, $J_{1,10}$=2.0 Hz, H_{10}, 1H), 5.74 (m, H_1, 1H), 5.48 (bs, H_8, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.61, 149.08, 141.76, 138.89, 127.92, 127.34, 122.88, 122.15, 89.01, 86.36. IR (KBr, cm^{-1}) 3055, 1600, 1472, 1395, 1268, 1063, 808.

Bromination of (1*S*(*R*),8*S*(*R*))-9-bromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (12) at 0°C

To a magnetically stirred solution of **12** (200 mg, 0.90 mmol) in 10 mL dry chloroform cooled to 0°C was added dropwise a solution of bromine (160 mg, 1.0 mmol) in 5 mL chloroform during 2 min. After stirring at reaction temperature for 1 h, the solution was allowed to warm to 20°C. The solvent was removed under reduced pressure. The oily residue was crystallised from chloroform/hexane (1/3) to give 244 mg (71%) of the rearranged tribromide **11**.

Bromination of (1*S*(*R*),8*S*(*R*))-9-bromo-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (12) at 77°C

2.0 g (9.0 mmol) **12** was dissolved in 50 mL of carbon tetrachloride in a 20 mL flask which was equipped with 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 (1.73 g, 14.31 mmol) in 30 mL of carbon tetrachloride during 5 min. The resulting reaction mixture was heated for 2 min at reflux temperature. After being cooled to room temperature the solvent was evaporated. The residue was chromatographed on silica gel (100 g) eluting with hexane/ethyl acetate in ratio 10:1. The first fraction consisted of the tribromide **19**, which was crystallised from methylene chloride/hexane (1/2).

(1*R*(*S*),8*S*(*R*),10*S*(*R*))-9,9,10-Tribromo-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2,4,6-triene (19). 1.92 g (56%). Colourless crystals, mp:140–141°C. [Found: C, 31.15; H, 1.92. $C_{10}H_7Br_3O$ requires C, 31.37; H, 1.84%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.57–7.31 (m, aromatic, 4H), 5.76 (bs, H_8, 1H), 5.46 (bs, H_1, 1H), 4.40 (s, H_{10}, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.13, 143.26, 130.99, 130.05, 126.10, 121.61, 95.31, 90.98, 64.77, 63.67. IR (KBr, cm^{-1}) 3004, 1472, 1217, 1191, 987, 910, 859, 782. The second fraction consisted of endo tribromide that was crystallised from methylene chloride/hexane (1/2).

(1*R*(*S*),8*S*(*R*),10*R*(*S*))-9,9,10-Tribromo-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2,4,6-triene (20). 1.27 g (37%). Colourless crystals, mp: 74–75°C. [Found: C, 31.18; H, 1.95. $C_{10}H_7Br_3O$ requires C, 31.37; H, 1.84 %]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49–7.28 (m, aromatic, 4H), 5.76 (s, H_8, 1H), 5.51 (d, $J_{1,10}$=4.8 Hz, H_1, 1H), 5.18 (d, $J_{1,10}$=4.8 Hz, H_{10}, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.01, 142.07, 130.06, 129.85, 125.64, 125.14, 94.16, 85.72, 63.94, 60.77. IR (KBr, cm^{-1}) 3004, 1472, 1265, 1217, 1165, 987, 961, 859, 834, 782.

Elimination of tribromide 19

To a stirred solution of tribromide **19** (3.0 g, 7.8 mmol) in dry and freshly distilled THF (50 mL) was added 1.32 g (11.7 mmol) of potassium *tert*-butoxide solution in THF (15 mL). The resulting reaction mixture was heated for 3 h at reflux temperature. After being cooled to room temperature the solvent was evaporated. The mixture was diluted with water and the aqueous solution was extracted with ether (3×50 mL), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was filtered on a short silica gel column (20 g) eluted with hexane/ethyl acetate (10:1) to give 2.08 g (88 %) of dibromide **21** as the sole product.

From the elimination of **20** under the same reaction condition, the dibromide **21** was obtained also as the sole product in ca. 90% yield.

9,10-Dibromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (21). Colourless crystals from methylene chloride/hexane 1/3, mp: 120°C. [Found: C, 39.69; H, 2.12. $C_{10}H_6Br_2O$ requires C, 39.78; H, 2.00 %]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43–7.06 (AA′BB′ system, aromatic, 4H), 5.59 (s, H_1, H_8, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.84, 135.93, 128.19, 122.69, 90.20. IR (KBr, cm^{-1}) 3080, 3055, 3029, 1600, 1472, 1446, 1246, 1242, 1063, 1012, 859, 782, 757.

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