# High Temperature Bromination. 7.[1] Bromination of Norbornadiene

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*Received February 2, 1996*

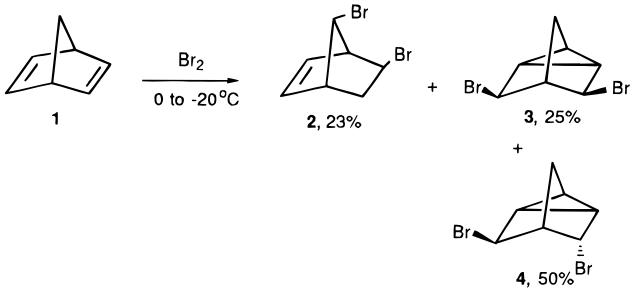
Constitution and configuration of the products formed by electrophilic addition to norbornene and norbornadienes are interesting.[2] The reaction of these systems have been used as a mechanistic probe to elucidate the mechanism of different reactions. The electrophiles add to norbornene preferentially (or exclusively) by exo-attack, while in norbornadiene there is possibility of both *exo* and *endo*-attack. Halogenation of norbornadiene[3] has been studied less intensively. Winstein[4] has studied bromination of norbornadiene and has pointed out the *dangerous properties* of the products.

Addition of bromine to norbornadiene at 0 to −20 °C in chlorinated solvents results in the products of Wagner−Meerwein rearrangement and homoallylic conjugation;[4] no products of *trans*-addition have been detected. The formation of halogenonium ion cannot compete with that of nonclassical ions. The formation of **2**−**4** can be rationalized in terms of initially formation of *exo*-attack (Scheme 1).

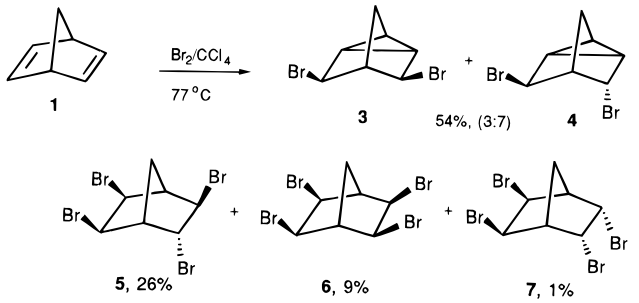
In the course of studying the bromination reactions of the unsaturated bicyclic systems we noticed that the reaction temperature has a dramatic influence on product distribution. Bromination at room and lower temperatures gives rearranged products via Wagner−Meerwein rearrangement with accompanying alkyl and aryl (in the case of benzannelated systems) migration. However, the bromination of these hydrocarbons at higher temperatures (80−150 °C) resulted in the formation of nonrearranged products.[5] High temperature bromination prevents skeletal rearrangement. In connection with our continuing work in the temperature bromination reactions[5] we have been interested in the bromination reaction of norbornadiene at high temperature in order to see the effect of the temperature on skeletal rearrangement and in the synthesis of disubstituted norbornadiene derivatives which opens up entry to further substituted norbornadiene derivatives.

Norbornadiene was submitted to high temperature bromination. To a refluxing solution of norbornadiene

**Scheme 1**




**Scheme 2**




in carbon tetrachloride was added a hot solution of bromine in carbon tetrachloride in one portion. The color of bromine disappeared immediately. After distillation of the reaction mixture followed by fractional crystallization and silica gel chromatography, we isolated five products, three of them with nonrearranged skeleton (Scheme 2).

Dibromo nortricyclanes **3** and **4** were formed in 54% total yield in a ratio of 3:7. The $^1$H NMR and especially the $^{13}$C NMR spectra are in good agreement with structures **3** and **4**. Besides these products we isolated three nonrearranged tetrabromo compounds **5**−**7** with norbornane structure. Carefully examination of the reaction mixture did not reveal the formation of any trace of Wagner−Meerwein rearrangement product **2**.

The determination of the exact structures **5**−**7** would allow us to propose the mechanism by addition of electrophiles to norbornadiene. The structural assignment to the tetrabromo compound **6** was achieved by means of proton and carbon NMR data. The $^1$H NMR and $^{13}$C NMR spectra of **6** were highly symmetrical according to the symmetry in the molecule. Especially, a three-line $^{13}$C NMR spectrum is in good agreement either for all *exo*- or all *endo*-configuration of the tetrabromides. The configuration of **6** has been confirmed by differential $^1$H NMR nuclear overhauser enhancement (NOE) studies. Irradiation of bridge methylene protons at $\delta$ 2.33 induces an enhancement only of the bridgehead protons not the methine protons where bromine atoms are attached, which clearly indicates the all *exo*-orientation of bromine atoms (Scheme 3).

The chemical shift of the protons on the bridging carbon are highly sensitive against the configuration of substituent attached to $C_2$, $C_3$, $C_5$, and $C_6$ carbon atoms. Any steric repulsion between methylene protons and substituents related to the van der Waals effect causes a paramagnetic contribution to the shielding constants of methylene protons which results in a shift to lower field.[6] The methylene protons of norbornane resonates at $\delta$ 1.21. *Exo*-orientation of two bromine atoms as in

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(1) For Part VI see: Daştan, A.; Balci, M.; Hökelek, T.; Ülkü, D.; Büyükgüngör, O. *Tetrahedron* **1994**, *50*, 10555−10578.
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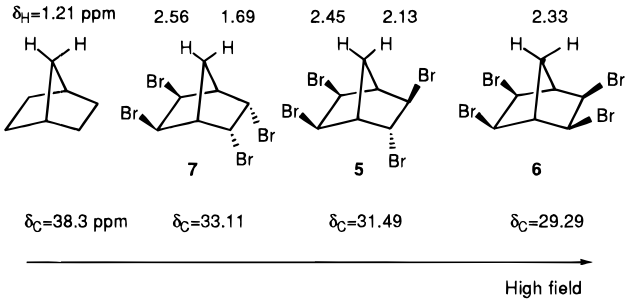
S0022-3263(96)00225-3 CCC: $12.00 

**Scheme 3**




the case of **7** causes a remarkable chemical shift difference of methylene protons ($\delta$ 1.69 and $\delta$ 2.56). However, the chemical shift difference is getting smaller in the case of *exo,endo*, *exo,exo*-orientation of tetrabromine atoms in **5**. On the basis of these chemical shifts we can also conclude the correct configuration of **5**. In saturated cyclic systems, the steric effect causes shielding of carbon resonances when two substituted carbon atoms are $\gamma$-gauche relative to each other. Halogens raise the $\gamma$-effect up to $-7$ ppm.[7] The high-field resonance of the methylene carbon in **6** compared to norbornane indicates clearly the all *exo*-orientation of bromine atoms. The trends of $^{13}C$ chemical shifts of the bridge carbons toward high field also nicely support the proposed structures.

In order to test whether tetrabromine compounds **5**−**7** are primary or secondary products which can be formed by reaction of nortricyclanes **3** and **4** with excess bromine at high temperature, we submitted nortricyclanes **3** and **4** to high temperature bromine reaction. We have determined that these products are stable in refluxing $CCl_4$ and in the presence of excess bromine.

All products isolated after high temperature bromination show no Wagner−Meerwein type rearranged products. It is evident from the bromine configuration in **5**−**7** that the initial attack by the bromine has occurred from the sterically less favored *exo*-side of the $\pi$-system. In the case of **7** there is also *endo*-attack to one of the double bonds. Giese and Kay have already observed an *endo*-attack in 5% yield during the radical addition of bromotrichloromethane to norbornadiene.[8]

Studies concerning the mechanism of *syn*-addition show that the *syn*-adduct can arise either from direct *syn*-collapse of an ion pair or from rotation followed by *anti*-collapse.[9] Because of the rigid skeleton in **1**, a bond rotation is out of the question. In this case, we assume that the high temperature bromination is occurring by a free radical mechanism. Radical intermediates are much less likely to rearrange. The fact that we do not observe any trace of Wagner−Meerwein rearranged products indicates that the *trans* addition of bromine in **5** can also arise from the radical intermediates.

Conducting the bromination reaction at reflux temperature of $CCl_4$ in the presence of free radical inhibitors like 2,4,6-tri-*tert*-butylphenol suppressed the formation

**Scheme 4**

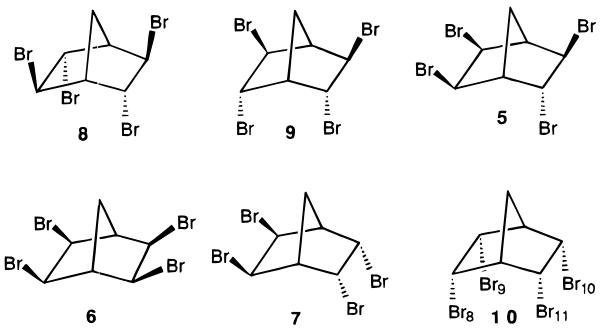



**Table 1. Strain Energies of Tetrabromo Norbornane Derivatives from the MM2 Force Field Calculations (energies in kcal/mol)**

| molecule | total | bond | angle | torsional | van der Waals | stretch-bend | electrostatic |
|---|---|---|---|---|---|---|---|
| 8 | 36.71 | 1.45 | 12.99 | 11.74 | 5.18 | -0.270 | 5.63 |
| 5 | 40.49 | 1.62 | 13.48 | 12.63 | 6.53 | -0.155 | 6.39 |
| 7 | 44.21 | 1.66 | 16.48 | 12.08 | 7.38 | -0.08 | 6.70 |
| 6 | 44.56 | 1.80 | 13.93 | 13.55 | 7.84 | -0.042 | 7.49 |
| 10 | 52.12 | 1.65 | 24.49 | 10.35 | 7.68 | -0.022 | 8.17 |

of the nonrearranged products. Rearranged product **2** and nortricyclanes **3** and **4** were formed in a yield of 85%. Careful 200 MHz $^1H$ NMR measurements did not reveal the formation of any trace of **5**−**7** with norbornane structure. Furthermore, when free radical inhibitors are added to bromination reaction at $-10$ °C, we obtained exactly the same product distribution as by the reaction in the absence of radical scavengers. On the basis of these observations, we can conclude that the reaction mechanism of bromination at 0−20 °C is ionic. Moreover, these observations support strongly the assumption that there is a competition between radical and ionic reactions at high temperatures. Tetrabromides **5**−**7** with nonrearranged norbornane structures are formed exclusively by a radical mechanism. If we compare the results obtained from the bromination reaction of norbornadiene at different temperatures we notice that molecular rearrangement is getting suppressed by going to higher temperatures.

Generally seven nonrearranged isomers can be expected from the reaction of bromine with norbornadiene (Scheme 4). The MM2 force field calculations[10] on some possible isomers indicate that the *endo,exo,endo,exo* isomer **8** has the most stable structure (36.7 kcal/mol total strain energy) whereas the *endo,endo,endo,endo* isomer **10** is of much higher energy as a consequence of cis orientation of bromine atoms which causes a strong dipole−dipole and van der Waals interactions.

Strong steric repulsion between the vicinal brom atoms in the case of *endo,endo* (or *exo,exo*) orientation can also be seen nicely between Br9 and Br10 (Br8 and Br11) atoms in **10**. The MM2 force field calculations show that the distances between Br8−Br9 (3.467 Å) and Br8−Br11-(3.476 Å) in **10** are not much different from each other. The important feature of this isomer **10** is a marked interaction between all four bromine atoms. The calculated strain energy of a value of 52 kcal/mol predicts the existence of this strong interaction and prevents the formation of this isomer. It is not surprising that this isomer was not detected under the reaction products. On the other hand, we were also not able to detect any trace

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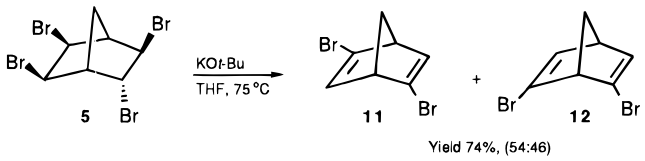
**Scheme 5**




of **8** and **9** in the reaction mixture after a careful search by NMR. Nonexistence of these thermodynamically most stable compounds forces us to assume that the first bromine attack to the double bond in norbornadiene takes place from the *exo*-face and in a *cis*-fashion. During the second addition, most stable compounds are formed preferentially in the following order **5** > **6** > **7**. Total strain energies of **6** and **7** indicate that the isomer **6** has slightly more strain than **7**. The fact that **6** and **7** was formed in a ratio of 9:1 indicates that *exo*-attack is preferred.

After successful synthesis and characterization of these nonrearranged products **5**−**7** which have the requisite skeletal arrangement and functionality to permit the easy introduction of two double bonds, we submitted either pure isomer **5** or an isomeric mixture consisting of **5**−**7** to a dehydrobromination reaction with 2 mol of potassium *tert*-butoxide and isolated **11** and **12** in a ratio of 54:46 (total yield 74%) which was separated by silica gel column chromatography eluting with petroleum ether (Scheme 5). Structural assignments to **11** and **12** were achieved by means of proton and carbon NMR data. A four-line $^{13}$C-NMR spectrum of **11** and a five-line $^{13}$C-NMR spectrum of **12** strongly supports the symmetrical structures. With the completion of the synthesis of **11** and **12**, we opened up an entry to nongeminal disubstituted norbornadiene derivatives.

## Experimental Section

**Precaution:** Norbornadiene bromides are dangerous compounds. Prof. S. Winstein has reported[4b] that of three co-workers who have used the norbornadiene dibromides, two later developed similar pulmonary disorders which contributed to their subsequent deaths. **General.** Commercial reagents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Solvents were concentrated at reduced pressure. Melting points are uncorrected. Infrared spectra were obtained from films on NaCl plates for liquids or from solution in 0.1 mm cells or KBr pellets for solids on a regular instrument. The $^1$H and $^{13}$C NMR spectra were recorded on 200 (50)- and 60-MHz spectrometers. Mass spectra (electron impact) were recorded at 70 eV as *m*/*z*. Column chromatography was performed on silica gel (60 mesh, Merck).

**Bromination of Norbornadiene (1) at 77 °C.** Norbornadiene **1** (3.2 g , 34.78 mmol) was dissolved in 30 mL of $CCl_4$ 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 a hot solution (65−70 °C) of bromine (8.79 g, 55 mmol) in 10 mL of carbon tetrachloride in one portion. The color of bromine disappeared immediately. The resulting reaction mixture was heated for 5 min at reflux temperature. After being cooled to room temperature, the solvent was evaporated. The oily residue (12.34 g) was dissolved in 40 mL of $CH_2Cl_2$−hexane (1:1) and allowed to stand for several days in a refrigerator. A 1.01 g (7%) amount of crystalline *exo*,*exo*,*exo*,*exo*-2,3,5,6-tetrabromonorbornane (**6**) was isolated. After filtration of the tetrabromide **6**, the organic solvent was evaporated, and the oily residue (10.83 g) was fractionated under reduced pressure. The distillate (bp 75−85 °C/10 mm) was identified as dibromonortricyclanes **3** and **4** (4.70 g, 54%) in a ratio of 31:69 (by NMR). A mixture of dibromonortricyclanes (550 mg) was chromatographed on silica gel (110 g) with *n*-hexane to give **3** (28 mg, 5%) and **4** (40 mg, 7%).

***exo*,exo-3,5-Dibromonortricyclane (3):**[4] colorless liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 3.97 (s, 2H, $H_3$ and $H_5$), 2.35 (s, 1H, $H_4$), 2.15 (s, 2H, $H_7$), 1.68 (m, 3H, $H_1$, $H_2$, and $H_6$); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 53.17, 46.24, 31.24, 24.45, 15.61.

***exo*,*endo*-3,5-Dibromonortricyclane (4):**[4] colorless liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.60 (s, 1H, $H_5$), 3.96 (s, 1H, $H_3$), 2.30 (s, 1H, $H_4$), 2.13 ($\delta$, $J$ = 11.4 Hz, 1H, $H_{7b}$), 1.80 (t, $J$ = 4.7 Hz, 1H), 1.66 (t, $J$ = 4.9 Hz, 1H), 1.57 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 56.50, 55.94, 46.08, 32.27, 24.27, 21.48, 17.63.

The distillation residue was filtered on a short silica gel column (10 g) eluted with petroleum ether−$CHCl_3$ (4:1) to give 5.70 g (40%) of crude product which was identified as tetrabromonorbornanes **5**−**7**. A part of the crude tetrabromonorbornanes (1.80 g) was chromatographed on silica gel (200 g). Elution with petroleum ether gave as the first fraction *exo*, *endo*,*exo*,*exo*-2,3,5,6-tetrabromonorbornane **5** (1.20 g, total yield: 26%): colorless crystals, mp 67−68 °C from chloroform/*n*-hexane (3:1); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.83 (dd, $J$ = 6.9, 2.1 Hz, 1H, $H_5$) 4.38 (tm, $J$ = 2.9 Hz, 1H, $H_3$), 4.22 (dd, $J$ = 6.9, 2.0 Hz, 1H, $H_6$), 3.86 (t, $J$ = 2.9 Hz, 1H, $H_2$), 2.84 (m, 2H, $H_1$ and $H_4$), 2.45 (dm, $J$ = 11.8 Hz, 1H, $H_{7b}$), 2.13 (dm, $J$ = 11.8 Hz, 1H, $H_{7a}$); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 57.64 ($C_5$), 57.44 ($C_3$), 55.55 ($C_6$), 54.23 ($C_2$), 52.10 ($C_1$), 51.64 ($C_4$), 31.49 ($C_7$); IR (KBr, cm$^{-1}$) 2970, 2950, 1440, 1300, 1230, 920, 850; MS *m*/*z* 408/410/412/414/416 ($M^+$, 22), 327/329/331/333 ($M^+$ − Br, 100), 249/251/253 ($M^+$ − 2Br, 30), 169/171($M^+$ − 3Br, 60), 91 ($M^+$ − 4Br, 67), 65 (50). Anal. Calcd for $C_7H_8Br_4$; C, 20.42; H, 1.96. Found: C, 20.52; H, 1.85.

Continued elution with the same solvent afforded *endo*, *endo*,*exo*,*exo*-2,3,5,6-tetrabromonorbornane (**7**) as the second fraction (35 mg, total yield: 1%): colorless crystals, mp 184−185 °C from chloroform/*n*-hexane (1:1); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.88 (d, $J$ = 2.0 Hz, 2H, $H_5$ and $H_6$), 4.50 (t, $J$ = 2.4 Hz, 2H, $H_2$ and $H_3$), 2.85 (m, 2H, $H_1$ and $H_4$), 2.56 (dt, $J$ = 11.8, 1.9 Hz, 1H, $H_{7b}$), 1.69 (br d, 1H, $H_{7a}$); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 54.93 ($C_2$ and $C_3$), 53.10 ($C_5$ and $C_6$), 52.43 ($C_1$ and $C_4$), 33.11 ($C_7$); IR (KBr, cm$^{-1}$) 2970, 1450, 1300, 1280, 1210, 1140, 910, 900; MS *m*/*z* 408/410/412/ 414/416 ($M^+$, 18), 327/329/331/333 ($M^+$ − Br, 100), 249/251/253 ($M^+$ − 2Br, 41), 169/171($M^+$ − 3Br, 69), 91 ($M^+$ − 4Br, 64), 65 (57). Anal. Calcd for $C_7H_8Br_4$; C, 20.42; H, 1.96. Found: C, 20.31; H, 1.83.

Further elution with $CH_2Cl_2$−petroleum ether (3:1) yielded *exo*, *exo*,*exo*,*exo*-2,3,5,6-tetrabromonorbornane (**6**) as the last fraction (80 mg, total yield: 9%): colorless crystals, mp 261−262 °C from chloroform; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.17 (br s, 4H, $H_2$, $H_3$, $H_5$, and $H_6$), 2.96 (br s, 2H, $H_1$ and $H_4$), 2.33 (br s, 2H, $H_7$ ); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 58.94 ($C_2$, $C_3$, $C_5$, and $C_6$), 52.40 ($C_1$ and $C_4$), 29.29 ($C_7$); IR (KBr cm$^{-1}$) 2970, 1450, 1310, 1270, 1150, 910, 850; MS *m*/*z* 408/410/412/414/416 ($M^+$, 16), 327/329/331/333 ($M^+$ − Br, 100), 249/251/253 ($M^+$ − 2Br, 46), 169/171 ($M^+$ − 3Br, 58), 91 ($M^+$ − 4Br, 56), 65 (51). Anal. Calcd for $C_7H_8Br_4$; C, 20.42; H, 1.96. Found: C, 20.15; H, 2.01.

**Bromination of Norbornadiene (1) in the Presence of 2,4,6-Tri-*tert*-Butylphenol at 77 °C.** To a solution of norbornadiene (100 mg, 1.08 mmol) and 2,4,6-tri-*tert*-butylphenol (600 mg, 2.29 mmol) in 3 mL of refluxing carbon tetrachloride was added a hot solution of bromine (346 mg, 2.16 mmol) in 0.35 mL of carbon tetrachloride in one portion. The color of bromine disappeared. After cooling to room temperature, the solvent was evaporated. NMR analysis of the residue indicated the formation of Wagner−Meerwein rearrangement product **2** and nortricyclane derivatives **3** and **4** in 85% yield.

**Bromination of Dibromonortricyclanes 3 and 4 at 77 °C.** To a solution of a mixture of dibromonortricylanes (0.44 g, 1.76 mmol) in 5 mL of refluxing carbon tetrachloride was added a hot solution of bromine (0.32 g, 2 mmol) in 1 mL of hot carbon tetrachloride in one portion. The resulting reaction mixture was refluxed for 0.5 h and cooled to room temperature, and the solvent was evaporated. NMR analysis of the residue indicated that the dibromonortricyclanes were not changed and are stabilized under the reaction conditions.

**Reaction of Tetrabromonorbornanes 5−7 with Potassium *tert*-Butoxide.** To a stirred solution of a mixture of tetrabromides **5**−**7** (1.64 g, 3.9 mmol) in dry and freshly distilled THF (40 mL) was added 1.23 g (10.9 mmol) of potassium *tert*-butoxide. The resulting reaction mixture was refluxed for 3 h and then cooled to room temperature. The mixture was diluted with water, and the aqueous solution was extracted with ether,

washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue (a pale yellow oil) was filtered on a short silica gel column (10 g) eluted with *n*-hexane to give 700 mg (70%) of crude 2,5- (**11**) and 2,6-dibromonorbornadiene (**12**) in a ratio of 52:48 (by NMR). The crude product (700 mg) was chromatographed on silica gel (110 g). Elution with petroleum ether gave 65 mg (6%) of pure 2,5-dibromonorbornadiene (**11**) as the first fraction. The other isomer, 2,6-dibromonorbornadiene (**12**), was not isolated in purity (purity over 95%).

**2,5-Dibromonorbornadiene (11):** colorless liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.80 (t, $J$ = 2.1 Hz, 2H, olefinic H), 3.51 (m, 2H, bridgehead H), 2.36 (m, 2H, bridge H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 139.85 (=*C*H), 138.53 (=*C*Br), 74.61 ($C_1$ and $C_4$), 61.63 ($C_7$); IR (film, cm$^{-1}$) 2950, 1600, 1575, 1300, 1200, 980, 850. Anal. Calcd for $C_7H_6Br_2$: C, 33.63; H, 2.42. Found: C, 33.21; H, 2.32.

**2,6-Dibromonorbornadiene (12):** colorless liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.71 (d, $J$ = 2.9 Hz, 2H, olefinic H), 3.60 (m, 1H, $H_1$), 3.47 (m, 1H, $H_4$), 2.35 (m, 2H, bridge H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 141.65 (=*C*H), 136.72 (=*C*Br), 74.80 ($C_1$), 67.71 ($C_4$), 54.84 ($C_7$).

The dibromonorbornadienes **11** and **12** were found to be unstable at room temperature. However, at low temperature (under −30 °C) or basic conditions, it can be kept for several days.

**Reaction of *exo,endo,exo,exo*-2,3,5,6-Tetrabromonorbornane (5) with Potassium *tert*-Butoxide.** The reaction was carried out as described above by using 1.11 g (2.7 mmol) of pure tetrabromide **5** and 0.75 g (6.75 mmol) of potassium *tert*-butoxide in 30 mL of dry THF, and 500 mg (74%) of 2,5- and 2,6-dibromonorbornadiene (**11, 12**) was obtained as an isomeric mixture. The relative percentage of products **11** and **12** was obtained from the integration of $^1$H NMR signals for the olefinic hydrogens and found to be in a 54:46 ratio for **11** and **12**, respectively.

**Acknowledgment.** The authors are indebted to the Department of Chemistry (Atatürk University) and the Department of Chemistry (Gaziosmanpaşa University Grant 1993/5) for financial support of this work and State Planning Organization of Turkey (DPT) for purchasing a 200 MHz NMR spectrometer.

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