Functionalization of Benzonorbornadiene: High-Temperature Bromination† and Electrochemical Oxidation

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The electrophilic addition of bromine to benzonorbornadiene (**1**) at 10 °C led in high yield to the formation of 2-*exo*-7-*anti*-dibromide **2**. However, high-temperature bromination in decalin at 150 °C resulted in the formation of five products, **2**–**6**, consisting of non-rearranged and rearranged products in a ratio of 8:2. Conducting the bromination reaction in the presence of a free radical inhibitor like 2,4,6-tri-*tert*-butylphenol suppressed the formation of the non-rearranged products. This very strongly supports the assumption that there is a competition between radical and ionic reactions. Anodic oxidation of benzonorbornadiene was investigated. Electrolysis of benzonorbornadiene in different solvents resulted in the formation of 2,7-disubstituted benzonorborn-5-ene derivatives, **8**–**11**, in good yields.

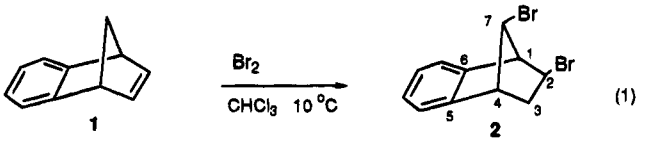
Introduction

Benzonorbornadiene (**1**) affords the possibilities of several mechanistically interesting investigations. Benzonorbornadiene (**1**) is an intriguing compound in view of the di-π-methane rearrangement[1] and solvolytic reactivity.[2]

In connection with our continuing work in the high temperature bromination reactions[3] we have been interested in the bromination reaction of benzonorbornadiene (**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 the product distribution. Bromination at room and lower temperatures give rearranged products via Wagner–Meerwein rearrangement with accompanying aryl and alkyl migration.[3] However, the bromination of these hydrocarbons at higher temperatures (80–150 °C) resulted in the formation of non-rearranged products. High-temperature bromination prevents skeletal rearrangement. As an extension of this work we have studied bromination reaction of benzonorbornadiene (**1**) at different temperatures.

Results and Discussion

Bromination of Benzonorbornadiene (1) at 10 °C. The electrophilic addition of bromine to benzonorbornadiene (**1**) was first reported by Wittig and Knauss to yield a dibromide **2**[4] in quantitative yield. At about the same time, the related addition of bromine to a diacetoxy derivative (substituted in the benzene ring) of **1**, which proceeded with a rearrangement, was described.[5] We also reacted benzonorbornadiene (**1**) with bromine in carbon tetrachloride solution at room temperature and isolated the 2-*exo*-7-*anti*-dibromide **2** in high yield as reported in the literature[4] (eq 1). Extensive NMR studies did not reveal the formation of any other products.



(1)

Complete peak assignments were made on the basis of extensive double resonance experiments. Methylene protons resonated as an AB-system at δ 2.90 and 2.22 and gave the most useful information. Irradiation of the resonances at δ 3.52 converted the signal at 2.90 ppm into a doublet of doublets and removed the line broadening of the signal at δ 2.22 to give a doublet of doublets of doublets. Therefore, this signal at δ 3.52 was assigned to the bridgehead proton H_4. There was no measurable coupling between H_4 and H_{3endo} due to a nearly 90° dihedral angle. Inspection of a Dreidings model confirmed this angle. The small splitting (J = 1.4 Hz) of the resonance at δ 2.22 arose from the H_7 proton. In the case of ^4J in the bicyclic systems one speaks of the M or W arrangement. The bonding arrangement of the coupled protons H_4 and H_{3endo} meets M criterion. Irradiation of the multiplet at δ 4.18 remove this long-range coupling. On the basis of these observations we made the correct assignments to bridge proton and methylene protons.

Wilt and Chenier[6] have studied radical addition of bromine to **1** by taking 1,2-dibromotetrachloroethane, an interesting bromine carrier, to brominate the allylic positions. This reagent would also add bromine to the double bond of an olefin. Indeed, quantitative addition of bromine to **1** via this reagent in carbon tetrachloride during irradiation with a sun lamp and under reflux gave 2,3-*trans*-dibromobenzonorborn-5-ene (**3**) and 2,3-*exo*-*cis*-dibromobenzonorborn-5-ene (**4**) in a ratio of 89:11. The rearranged product **2** was not isolated.

Bromination of Benzonorbornadiene (1) at 150 °C. For the high-temperature bromination reaction, a hot solution of bromine in decalin was added to a solution of **1** in decalin at 150 °C in one portion. We isolated five

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(5) Meinwald, J.; Wiley, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 3667.

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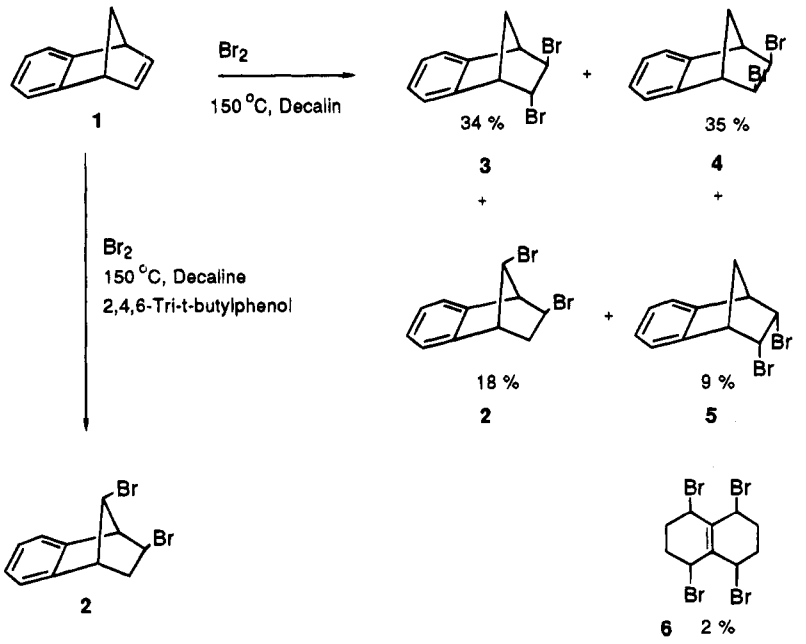
Scheme 1

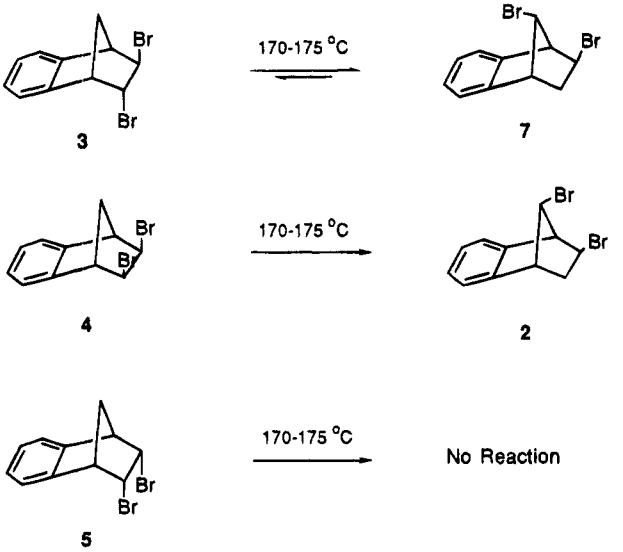


products, **2**–**6**, in yields of 18, 34, 35, 9, and 2%, respectively (Scheme 1).

The structures of these compounds have been elucidated on the basis of ^{1}H NMR and ^{13}C NMR and extensive double resonance experiments and by comparison of the spectral data with those reported in the literature.[7] Symmetrical *endo-cis*-isomer **5** has been observed for the first time. The ^{1}H NMR spectrum of this isomer reveals sufficient information for tentative assignments to be made. Compound **5** exhibits AA′BB′ and AA′XX′ systems arising from the aromatic, bridgehead, and CHBr protons which indicate clearly the symmetrical structure and *syn* addition of bromine. The *endo* stereochemical assignment for the bromine atoms is supported by the absence of a coupling between CHBr protons and the methylene proton *syn* to the benzene ring. This coupling can be seen in the case of **4** (W-orientation). Furthermore, a six-line ^{13}C NMR is also in good agreement with the proposed structure. Additionally, we isolated a tetrabromo compound, **6**,[8] which is derived from solvent. ^{1}H and ^{13}C NMR spectra of **6** indicates the formation of a highly symmetrical compound whose configuration is not known.

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. This could explain also our stereochemical results. Conducting the bromination reaction in the presence of free radical inhibitors like 2,4,6-tri-*tert*-butylphenol suppressed the formation of the non-rearranged products. This very strongly supports the assumption that there is a competition between radical and ionic reactions.

Scheme 2



In order to test, whether the isolated compounds **2**–**5** formed by high-temperature bromination are primary or secondary products, we reacted them under the given reaction conditions and observed that all products **2**–**5** are stable. However, prolonged heating of **3** at 170–175 °C resulted in an equilibrium established between **3** and **7** with a ratio of 45:55 (Scheme 2). The same ratio was obtained by heating pure **7** at the same temperature. Compound **7** was separated by column chromatography and fully characterized.[10] Differential ^{1}H NMR-NOE measurements support this proposed structure. Irradiation at the resonance frequency at δ 4.85 caused enhancement of the signals for bridgehead protons and for the *exo*-methylene proton resonating at δ 2.47. This NOE

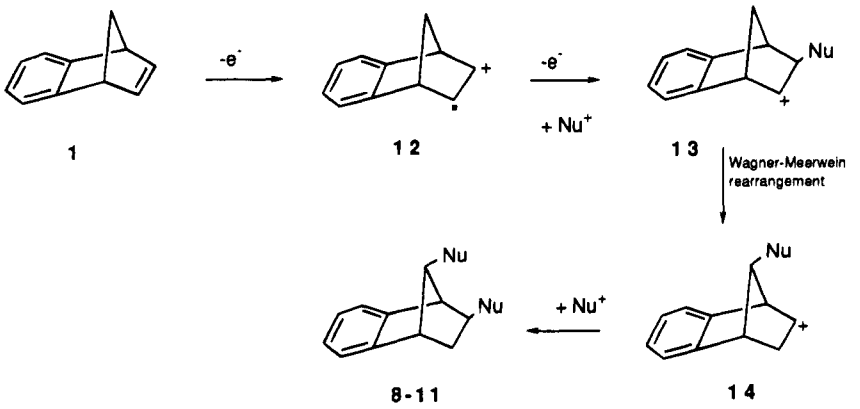
(7) For ^{1}H NMR spectra of some disubstituted benzonorborn-5-enes see: Cristol, S. J.; Nachtigal, G. W. *J. Org. Chem.* **1967**, *32*, 3727.

(8) Tetrabromo compound **6** has been synthesized by the bromination of decalin in liquid bromine in the presence of catalytic amounts of hydrobromic acid. Stetter, H.; Tresper, E. *Chem. Ber.* **1971**, *104*, 71.

(9) Heasley, G. H.; Bower, T. R.; Dougharty, K. W.; Easdon, J. C.; Heasley, V. L., Arnold, S.; Carter, T. L.; Yaeger, D. B.; Gipe, B. T.; Shellhamer, D. F. *J. Org. Chem.* **1980**, 45, 5150.

(10) Wilt and Chenier (ref 6) have reported the formation of **7** by refluxing **2** in hydrobromic acid. **7** could not be isolated. Extracted NMR data do not match with our ^{1}H NMR data.

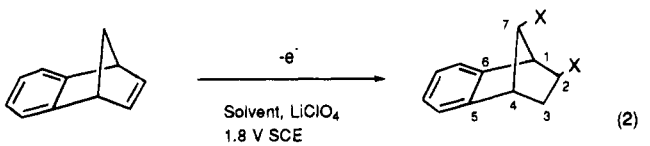
Scheme 3



experiment revealed exactly the *anti*-orientation of bridge proton H_7 and *endo*-orientation of H_2 proton and located the *exo* methylene protons. The ^{13}C NMR spectrum of this compound has 11 ^{13}C lines, this ruling out a symmetrical structure. Heating **4** at 170–175 °C gave the Wagner–Meerwein rearrangement product **2** in 93% yield as expected (Scheme 2). On the other hand, *endo-cis*- dibromide **5** did not show any tendency for rearrangement involving aryl shift because of the *endo* orientation of the bromine atoms. Alkyl-shift rearrangement is also prevented because of the possible formation of a highly strained four-membered ring.

On the basis of these results we assume that products **2–5** formed by bromination of benzonorbornadiene at 150 °C are primary products. High-temperature bromination of benzonorbornadiene gives more non-rearranged products than benzobarrelene.[11]

Electrochemical Oxidation of Benzonorbornadiene (1). For further functionalization of benzonorbornadiene we have studied electrochemical oxidation of **1**. The anodic oxidation[12] of benzonorbornadiene has been used as the key reaction to synthesize a variety of substituted benzonorborn-5-ene systems. All of the reactions were performed at room temperature using Pt-electrodes in appropriate solvents; the supporting electrolyte was lithium perchlorate. We obtained in all cases 2-*exo*-7-*anti*-disubstituted benzonorborn-5-ene derivatives



(2)

8 : X = OMe
9 : X = OEt
10 : X = OAc
11 : X = OH

8–11 which were isolated in good yields (eq 2). All compounds have been fully characterized by ^1H and ^{13}C NMR measurements and the signal assignments were made by extensive double resonance experiments and comparison of the spectra with those of **2**.

Benzonorbornadiene (**1**) has a nonconjugated diene system. Shono[13] has reported that this kind of system can undergo two types of reactions. Type A: one electron can be removed from one double bond to yield a radical cation followed by transannular reaction of the radical cation with another double bond to form a new carbon–carbon bond. Type B: allylic substitution[14] or oxidative addition at one double bond can occur without the intramolecular interaction. In our case, we do not observe any products involving type B mechanism. Involvement of the other double bond (type A mechanism) is out of the question since it is a part of an aromatic system. Otherwise we should observe nortricyclene-type products which would cause loss of aromaticity. All isolated products are Wagner–Meerwein type products where the involvement of the σ-bond in transannular interaction is dominant. Therefore, the formation of disubstituted benzonorborn-5-ene derivatives **8–11** can be rationalized by the following mechanism (Scheme 3).

We assume that the initiating reactive species is the radical cation **12** formed from a one-electron oxidation of the substrate. Subsequently, removing a second electron and nucleophilic attack of the solvent can form the cation **13** which undergoes Wagner–Meerwein rearrangement. Capture of the cation **14** by a solvent molecule can give products **8–11.**

Experimental Section

General. 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 ^1H and ^{13}C NMR spectra were recorded on 200 (50)- and 60-MHz spectrometers. Apparent splittings are given in all cases. Mass spectra (electron impact) were recorded at 70 eV as *m/z*. 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 aluminum plates. For electrochemical reactions, a potentiostat was used as a current source and all reactions were carried out at a controlled potential. Prior to use the electrodes and cells were cleaned with dichromate solution, rinsed with water, and dried. Nitrogen was bubbled through the cell before measurements.

Caution: It has been reported that of three laboratory workers who had used dibromides and bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders which contributed to their subsequent deaths.[16] The third exhibited minor skin sensitivity reactions. In the case of dibromides derived from benzonorbornadiene there is no report in the literature about the toxicological effect.[1] However, we recommend that the compounds be handled only with extreme caution.

(11) High-temperature bromination of benzobarrelene gives more rearranged products. Balci, M.; Daştan, A. Submitted for publication.
(12) For a review see: Shono, T. *Tetrahedron* **1984**, *40*, 811.
(13) (a) Shono, T.; Ikeda, A.; Hayashi, J.; Hakozaki, S. *J. Am. Chem. Soc.* **1975**, *97*, 4261. (b) Shono, T.; Ikeda, A. *J. Am. Chem. Soc.* **1972**, *94*, 7892.
(14) Usually electrochemical oxidation of olefins can form easily allylic cation. Since benzonorbornadiene system has a less reactive allylic hydrogen, transannular interactions play a dominant role.

Bromination of Benzonorbornadiene (1) at 10 °C. Synthesis of 2-*exo*-7-*anti*-Dibromobenzonorborn-5-ene (2). To a magnetically stirred solution of benzonorbornadiene (**1**) (300 mg, 2.1 mmol) in 10 mL of dry chloroform cooled to 10 °C was added dropwise a solution of bromine (368 mg, 2.30 mmol) in 5 mL chloroform during 5 min. After completion of the addition, the solution was allowed to warm to 20 °C. The solvent was removed under reduced pressure. The residue was crystallized from ethanol to give the rearranged dibromide **2** (632 mg, 99%): mp 76–77 °C, colorless crystals from ethanol (lit. mp 76–77 °C,[4c] 78–79 °C,[7,4a] 77–77.5 °C[5]); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15–7.29 (m, 4H, aryl), 4.18 (p, $J_{17} = J_{47} = J_{27} = J_{3endo7} = 1.4$ Hz, H_7), 3.82 (ddd, $J_{23endo} = 8$ Hz, $J_{23exo} = 4.5$ Hz, H_2), 3.77 (m, H_1), 3.52 (m, H_4), 2.90 (A-part of AB system, dt, $J_{3endo3exo} = 13.5$ Hz, $J_{3exo4} = 4.3$ Hz, H_{3exo}), 2.22 (bdd, B-part of AB system, H_{3endo}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.6, 143.0, 127.9, 127.3 , 121.8, 121.4, 56.5, 55.6, 51.1, 45.2, 36.6; MS (70 eV) *m*/*z* 300/302/304 (M^+, 2), 221/223 ($M^+ - Br$, 24), 141/142 ($M^+ - 2Br$, 86), 129 (naphthalene, 23), 115 (indenyl cation, 100); IR (KBr, cm^{-1}) 3065, 3020, 2980, 1460, 1435, 1278, 1258, 1245, 1015, 890, 835.

Bromination of Benzonorbornadiene (1) at 150 °C. Benzonorbornadiene (**1**) (300 mg, 2.1 mmol) was dissolved in 25 mL of decalin in a 50 mL two-necked flask equipped with reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet glass tube was connected to a 2 mL roundbottom flask which contained 368 mg (2.30 mmol) bromine. Bromine vapors obtained by heating the flask to 100 °C were transferred directly to decalin solution at a temperature of 150 °C over 5 min while stirring magnetically. The color of bromine disappeared immediately. The solvent was removed under reduced pressure; 637 mg of oily residue was chromatographed on silica gel (l00 g) eluting with hexane. Five compounds were isolated: **6** (11 mg, 2%), **3** (217 mg, 34%), **4** (223 mg, 35%), **2** (115 mg, 18%), and **5** (51 mg, 8%) in that order.

1,4,5,8-Tetrabromo-1,2,3,4,5,6,7,8-octahydronaphthalene (6): colorless crystals, mp 185.5–186 °C from chloroform/*n*-hexane 1:2 (lit. 188.6 °C,[15] 188–189 °C;[8] ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.16 (d, $J = 2.7$ Hz, 4H, H_1, H_4, H_5, and H_8), 2.10–2.60 (AA'BB' system, 8H, H_2, H_3, H_6, and H_7); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.5, 49.5, 28; MS (70 eV) *m*/*z* 375/373/372/371 ($M^+ - Br$, 8), 292/291/289 ($M^+ - 2Br$, 8), 213/211 ($M^+ - 3Br$, 27), 131/129/128 ($M^+ - 4Br$, naphthalene, 100); IR (KBr, cm^{-1}) 2955, 2905, 2835, 1423, 1335, 1200, 1170, 1000, 895, 743.

2,3-*trans*-Dibromobenzonorborn-5-ene (3): colorless liquid: ^{1}H NMR (200 MHz, $CDCl_3$) 7.25–7.31 (m, 4H, aryl) 4.72 (t, $J_{23} = J_{34} = 3.0$ Hz, H_3), 3.85 (m, H_2), 3.61 (m, H_1), 3.57 (m, H_4), 2.48 (bd, A-part of AB system, $J_{7syn7anti} = 10$ Hz, H_{7anti}), 2.25 (bd, B-part of AB system, H_{7syn}); ^{13}C NMR (50 MHz, $CDCl_3$) ppm 143.7, 143.3, 127.3, 126.8, 124.5, 121.7, 57.2, 56.8, 53.7, 52.1, 46.6; IR (NaCl, film, cm^{-1}) 3070, 3047, 3025, 2980, 2945, 2870, 1490, 1470, 1460, 1277, 1242, 1170, 760.

2,3-*exo*-*cis*-Dibromobenzonorborn-5-ene (4): mp 78–79 °C, colorless crystals from dichloromethane/*n*-hexane, 1:4; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.13–7.27 (AA'BB' system, 4H, aryl), 4.11 (d, $J_{27syn} = J_{37syn} = 2.1$ Hz, H_2 and H_3), 3.58 (t, $J_{17anti} = J_{17syn} = J_{47anti} = J_{47syn} = 1.5$ Hz, H_1 and H_4), 2.58 (dt, A-part of AB system, $J_{7syn7anti} = 9.9$ Hz, H_{7anti}), 2.05 (bd, B-part of AB system, H_{7syn}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.7, 127.5, 122.1, 54.9, 54.2, 45.1; MS (70 eV) *m*/*z* 300/302/304(M^+, 3), 221/223 ($M^+ - Br$, 56), 141/142 ($M^+ - 2Br$, 100), 128 (naphthalene, 4), 115 (indenyl cation, 63); IR (KBr, cm^{-1}) 2990, 2975, 2940, 1465, 1273, 1258, 1235, 1200, 960, 880, 760, 750.

2-*exo*-7-*anti*-Dibromobenzonorborn-5-ene (2): 115 mg, 18%. For physical data see above.

2,3-*endo*-*cis*-Dibromobenzonorborn-5-ene (5): mp 125–126 °C, colorless crystals from dichloromethane/*n*-hexane, 1:4; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.21–7.35 (AA'BB' system, 4H, aryl), 4.72 (m, H_2 and H_3), 3.57 (m, 2H, H_1 and H_4), 2.17 (bd, A-part of AB system, $J_{7syn7anti} = 10.1$, H_{7syn}), 1.85 (bd, B-part of AB system, H_{7anty}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.0, 126.4, 124.2, 52.8, 51.4, 47.3; MS (70 eV) *m*/*z* 300/302/304 (M^+, 5), 221/223 ($M^+ - Br$, 66), 141/142 ($M^+ - 2Br$, 100), 128 (naphthalene, 7), 115 (indenyl cation, 68); IR (KBr, cm^{-1}) 3010, 2950, 2920, 1470, 1457, 1318, 1241, 1200, 938. Anal. Calcd for $C_{11}H_{10}Br_2$: C, 43.75; H, 3.34. Found: C, 43.62, H, 3.25.

Bromination of Benzonorbornadiene (1) in the Presence of Free Radical Inhibitor at 150 °C. To a solution of benzonorbornadiene (**1**) (300 mg, 2.11 mmol) and 2,4,6-tri-*tert*-butylphenol (1.17 g, 4.43 mmol) in 25 mL of decalin was added a hot solution of bromine (368 mg, 2.30 mmol) in 5 mL of decalin at 150 °C while stirring magnetically. The solvent was removed under reduced pressure (20 Torr). The oily residue (600 mg) was chromatographed on silica gel (30 g) eluting with hexane. After recovery of 2,4,6-tri-*tert*-butylphenol and 108 mg of unreacted benzonorbornadiene, the rearranged product **2** (383 mg, 60%) was isolated as the sole product.

Thermal Rearrangemet of *trans*-Dibromide 3. Synthesis of 2-*exo*-7-*syn*-Dibromobenzonorborn-5-ene (7). An amount of 100 mg of *trans*-dibromide **3** was heated at 170 °C (without solvent) for 65 h. ^{1}H NMR analysis of the oily residue revealed that the mixture consisted of two isomeric compounds. This ratio was not changed after prolonged heating. Chromotography on silica gel eluting with hexane gave as the first fraction the starting material in 45% yield. The second fraction afforded the isomeric dibromide **7** (55 mg 55%): mp 87 °C colorless crystals from choloroform–hexane 1:4; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.18–7.33 (m, aryl, 4H,), 4.85 (t, $J_{17} = J_{47} = 1.5$, H_7), 3.90 (dd, $J_{23endo} = 8.4$ Hz, $J_{23exo} = 3.2$ Hz, H_2), 3.75 (m, H_1), 3.55 (bd, $J_{3exo4} = 3.8$, H_4), 2.47 (dt, A-part of AB system, $J_{3endo3exo} = 13.6$ Hz, H_{3exo}), 2.22 (dd, B-part of AB system, H_{3endo}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.5, 141.7, 128.3, 127.6, 124.2, 123.1, 63.4, 60.8, 52.1, 46.5, 40.1; IR (KBr, cm^{-1}) 3060, 2985, 2950, 1463, 1440, 1293, 1255, 830, 755. Anal. Calcd for $C_{11}H_{10}Br_2$: C, 43.75; H, 3.34. Found: C, 44.32, H, 3.19.

2-*exo*-7-*syn*-Dibromobenzonorborn-5-ene (7) was heated under the same reaction conditions as described for **3** and the same equilibrium mixture was formed.

Thermal rearrangement of *exo*-*cis*-Dibromide (4). An amount of 100 mg of *exo*-*cis*-dibromide **4** was heated at 170 °C (without solvent) for 13 days. The oily residue was chromatographed on 10 g of silica gel eluting with hexane to afford 2-*exo*-7-*anti*-dibromobenzonorborn-5-ene (93 mg 93%).

General Procedure for Electrochemical Oxidation of Benzonorbornadiene 1. Preparative electrolyses were carried out according to the following procedure. Into a 50 mL three-electrode H-cell fitted with Pt electrodes were placed approximately 0.7 mmol of benzonorbornadiene and 12 mmol of lithium perchlorate ($LiClO_4$) as electrolyte and 30 mL of the appropriate solvent. After 10.7 faradays/mol of electricity had been passed at a constant current of 0.2 A (1 h, terminal voltage:1.8 V (SCE)) through the solution, the anode solution was concentrated at reduced pressure. A volume of 100 mL of aqueous $NaHCO_3$ was added to the reaction mixture and the organic portion extracted with $CHCl_3$ (40 mL × 3). The extract was dried over $MgSO_4$ and the solvent removed in vacuo.

2-*exo*-7-*anti*-Dimethoxybenzonorborn-5-ene (8). Electrolysis was carried out in methanol. The residue was chromatographed on silica gel (50 g) eluting with *n*-hexane/ethyl acetate (95:5) to afford dimethoxy compound **8**: Colorless oil, (131 mg, 91%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10–7.30 (m, 4H, aryl), 3.61(br. s, H_7), 3.55 (br. s, H_1), 3.38 (br. s, 2 CH_3) 3.31–3.45 (m, H_2, H_4), 2.07 (dt, A-part of AB system, $J_{3endo3exo} = 12.2$ Hz, $J_{23exo} = J_{3exo4} = 3.6$ Hz, H_{3exo}), 1.83 (dd, B-part of AB system, $J_{23endo} = 7.3$ Hz, H_{3endo}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.7, 142.2, 127.2, 126.8, 122.8, 122.3, 92.5, 84.2, 58.1, 57.1, 49.9, 45.9, 33.2; MS (70 eV) *m*/*z* 204 (M^+, 7), 172 ($M^+ - CH_3OH$, 41), 157($M^+ - CH_3OH - CH_3$, 6), 128/129 (naphthalene, 23), 115/116 (indenyl cation, 23), 75; IR (NaCl, film, cm^{-1}) 3023, 2980, 2926, 2875, 2820, 1740, 1463, 1198, 1115, 1110. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 75.83 , H, 7.39.

2-*exo*-7-*anti*-Diethoxybenzonorborn-5-ene (9). An amount of 100 mg (0.7 mmol) benzonorbornadiene (**1**) was electrolyzed in 30 mL of ethanol as described above. The residue was chromatographed on silica gel (90 g) eluting with

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hexane/ethyl acetate (97:3) to afford diethoxy compound **9**: Colorless oil (103 mg, 63%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10–7.30 (m, 4H, aryl), 3.71(br. s, H_7), 3.45–3.67 (m, OCH_2, H_1 and H_2), 3.3 (m, H_4), 2.12 (dt, A-part of AB system, $J_{3endo3exo}$ = 12.0 Hz, J_{23exo} = J_{3exo4} = 3.7Hz, H_{3exo}), 1.78 (dd, B-part of AB system, J_{23endo} = 7.2, H_{3endo}), 1.22 (t, J_{CH2CH3} = 7.0 Hz, $-CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.0, 142.4, 127.0, 126.6, 122.8, 122.2, 90.4, 81.8, 65.3, 64.4, 50.3, 46.9, 33.7,16.0, 15.7; IR (NaCl, film, cm^{-1}) 3020, 2975, 2940, 2870, 1465, 1370, 1195, 1120. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 76.90, H, 8.09.

2-*exo*-7-*anti*-Diacetoxybenzonorborn-5-ene (10). 200 mg (1.4 mmol) benzonorbornadiene was electrolyzed in 30 mL acetic acid in the presence of sodium acetate (0.4 M) as electrolyte as described above. The residue was chromatographed on silica gel (60 g) eluting with *n*-hexane/ethyl acetate (95:5). The first fraction eluted was unreacted starting material **1** (100 mg), followed by diacetoxy compound **10**: Colorless crystals (128 mg, 70%), mp 80.5–81 °C from dichloromethane/*n*-hexane (1:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10–7.30 (m, 4H, aryl), 4.71 (dd, J_{23endo} = 7.3 Hz, J_{23exo} = 3.3 Hz, H_2), 4.66 (br. s, H_7), 3.71 (m, H_1), 3.41 (m, H_4), 2.14 (dt, A-part of AB system, $J_{3endo3exo}$ = 12.7 Hz, J_{3exo4} = 3.6 Hz, H_{3exo}), 2.10 (s, CH_3) 2.05 (s, CH_3), 2.00 (dd, B-part of AB system, H_{3endo}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.1, 171.0, 144.2, 139.9, 128.0, 127.5, 123.7, 122.2, 83.7, 75.7, 51.2, 46.1, 34.3, 21.7, 21.5; IR (CCl_4, cm^{-1}) 3030, 2990, 2950, 1740, 1360, 1365, 1228, 1050. Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.75, H, 6.01.

2-*exo*-7-*anti*-Hydroxybenzonorborn-5-ene (11). An amount of 200 mg (1.4 mmol) benzonorbornadiene (**1**) was electrolyzed in 30 mL of acetonitrile and 0.6 mL of water and in the precence of lithium perchlorate (12 mmol) as electrolyte in an unseparated electrolysis cell, where the anode was graphite and the cathode was Pt. After 2.1 faradays/mol of electricity had been passed at a constant current of 16 mA (5 h, the cell voltage was 5.1 V) through the solution, the cell solution was concentrated at reduced pressure. The residue was chromatographed on silica gel (90 g) eluting with *n*-hexane/ethyl acetate (90:10). The first fraction eluted was unreacted starting material **1** (40 mg), followed by dihydroxy compound **11**: colorless powder (67 mg, 34%), mp 70–71 °C from dichloromethane/*n*-hexane (1:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.08–7.27 (m, 4H, aryl), 4.28 (m, OH), 4.11 (m, H_7), 3.99 (m, H_2), 3.31 (m, H_1 and H_4), 2.10 (dt, A-part of AB system, $J_{3endo3exo}$ = 12.9 Hz, J_{3exo4} = J_{23exo} = 3.2 Hz, H_{3exo}), 1.96 (dd, B-part of AB system, J_{23endo} = 6.9 Hz, H_{3endo}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.0, 141.0, 127.3, 126.8, 123.2, 122.1, 85.6, 75.3, 55.1, 48.9, 37.0; MS (70 eV) m/z 158 ($M^+ - H_2O$, 39), 128/129/130 (naphthalene, 100), 115/116 (indenyl cation, 66); IR (KBr, cm^{-1}) 3350, 3016, 2935, 1460, 1420, 1193, 1063, 750. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.06, H, 6.53.

2-*exo*-7-*anti*-Dihydroxybenzonorborn-5-ene (11) from Hydrolysis of 10. An amount of 130 mg (0.5 mmol) of diacetoxy compound **10** was dissolved in 10 mL of anhydrous methanol. While dry NH_3 is being passed through solution, the mixture was stirred for 24 h at room temperature. Evaporation of solvent and formed acetamide gave 2-*exo*-7-*anti*-dihydroxybenzonorborn-5-ene (**11**) (73 mg, 83%). The isolated compound was identical with that obtained directly by electrolysis of benzonorbornadiene as reported above.

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