Rearrangement of Bicyclo[2.2.2]octa-2,5-diene and Bicyclo[3.2.2]nona-6,8-diene under the Conditions of Bromination

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A reaction of electrophilic bromination of norbornadiene homologs such as bicyclo[2.2.2]octa-2,5-diene (**4**) and bicyclo[3.2.2]nona-6,8-diene (**7**) with bromine gave hitherto unknown skeleton rearranged dibromides. The rearrangement may proceed via a bromonium cation of starting diene to give bicyclo[3.2.1]octene or bicyclo[3.3.1]nonene skeleton in respective cases. The observed rearrangement reactions are also confirmed in 6,7-bis(methoxycarbonyl) derivatives of bicyclodiene **7** under similar conditions.

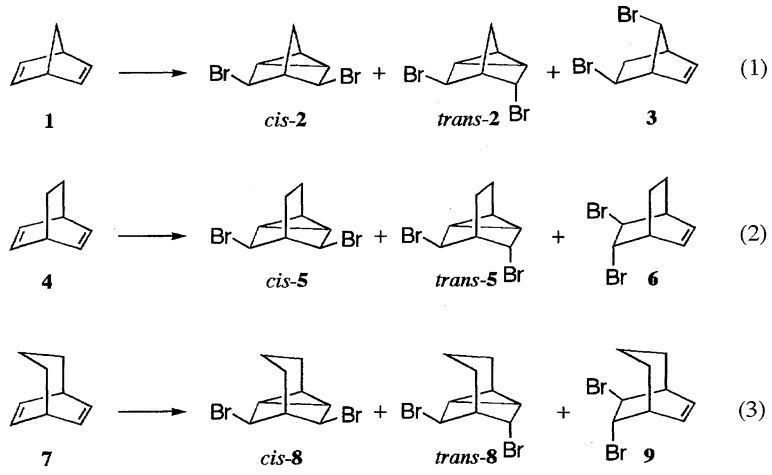
Addition of bromine to norbornadiene (**1**) has been explained as an electrophilic *exo*-facial attack leading to a hypothetical *homo*-conjugated adducts *cis*- and *trans*-**2** (1,5-addition product) and a skeleton rearrangement product **3** (Eq. 1).[1] A significant difference in the chemical behavior between norbornadiene and its homologs, such as bicyclo[2.2.2]octa-2,5-diene (**4**)[2] and bicyclo[3.2.2]nona-6,8-diene (**7**),[3] had been observed in the bromination reaction using bromine in dichloromethane or in carbon tetrachloride. Previously reported results for the bromination reaction of bicyclodienes **4** (Eq. 2)[4] and **7** (Eq. 3)[5] were 1,5-addition and 1,2-addition to the common cyclohexa-1,4-diene part in the molecule in both cases. That is to say, the bicyclodiene **4** gave the dibromides **5** and **6**, and the bicyclodiene **7** gave the dibromides **8** and **9** without any skeleton rearrangement products (Scheme 1).

In our synthetic work for norbornadiene homologs[6] such as bicyclo[4.2.2]deca-7,9-diene or bicyclo[5.2.2]undeca-8,10-diene in order to investigate a systematic change in features of mutual intramolecular interactions of the 1,4-cyclohexadiene part by changing the bridged methylene-chain length, we reinvestigated the present reaction of bicyclodienes **4** and **7**. We present here alternative results including the carbon skeleton rearrangement for the reaction reported before.

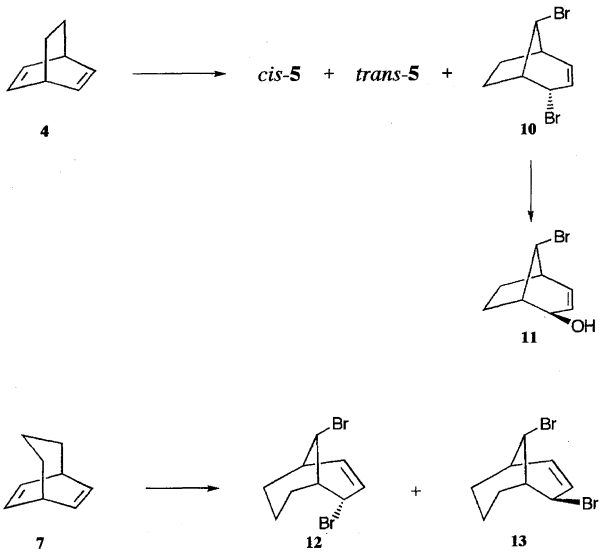
Results and Discussion

When a mixture of bicyclodiene **4** and a standard solution of bromine (see Experimental) was stirred in dichloromethane at 0 °C for 3 h, two kinds of already known 1,5-addition products *cis*- and *trans*-**5**, together with a hitherto unknown skeleton rearranged dibromide, (1*RS*,4*SR*,5*RS*,8*SR*)-4,8-dibromobicyclo[3.2.1]oct-2-ene (**10**), were recognized by ^{1}H NMR spectra of the reaction mixture. A preparative medium-pressure liquid chromatography (MPLC) using silica-gel column of the reaction mixture gave *trans*-**5**, **10**, and (1*RS*,4*RS*,5*SR*,8*SR*)-8-bromo-4-hydroxybicyclo[3.2.1]oct-2-ene (**11**), which is considered to be hydrolyzed product of **10** under the silica-gel column conditions, in 32, 20, and 3% yields. The dibromide *cis*-**5** could not be isolated under the conditions. The structure of the dibromide **10** was clearly distinguished from already reported 1,2-addition products such as **6** by inspection of the 2D-COSY spectrum[7] from following points: vicinal couplings between *ipso*-proton of one of the bromine C8-H (δ = 4.19) and two bridge-head methine protons C1–H and C5–H (δ = 2.59 and 2.63) were observed, while the olefinic proton C2–H (δ = 5.78) showed vicinal coupling with C1–H, coupling between olefinic proton C3–H (δ = 5.67) and the other bridge-head proton C5–H was absent. Additionally, the two contour plots at olefinic proton C3–H (δ = 5.67) and bridge-head proton C5–H by the other *ipso*-proton of bromine C4–H (δ=5.37) confirm the structure of **10** as indicated on Scheme 2. A selective decoupling experiment at C8–H revealed the coupling constant between C8–H and C2–H (J = 1.6 Hz) as a long range spin–spin coupling (W letter coupling), because the torsion angles H–C8–C1–C2 as 175.4° and C8–C1–C2–H as −144.5° were estimated for **10** by MNDO[8] structure optimization calculation. Thus the *endo*-configuration of bromine atom at C8 is suggested by an observation of a long range coupling. The stereochemistry of bromine atom at C4 is presumed to be the structure represented in Scheme 2 from a comparison of the chemical shift of C4–H with the corresponding proton of analogous compounds (**12** and **15**) whose details are described later.

Under similar conditions, bicyclodiene **7** gave two skeleton rearranged dibromides (1*RS*,4*SR*,5*RS*,9*SR*)- and (1*RS*,4*RS*,5*RS*,9*SR*)-4,9-dibromobicyclo[3.3.1]non-2-enes (**12** and **13**) in 40 and 39% yields, without any 1,5- and 1,2-addition products such as **8** and **9**. Structure of **12** and **13** were also confirmed by inspection of vicinal coupling information on the dibromocylohexene part from their 2D-COSY spectra.

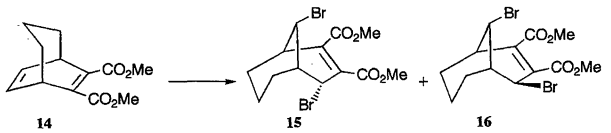


Scheme 1.



Scheme 2.

The *endo*-configuration of bromine atom at C9 was determined on the basis of W letter couplings ($J = 1.8$ Hz for **12** and $J = 1.5$ Hz for **13**) between C9–H ($\delta = 4.49$ for **12** and $\delta = 4.41$ for **13**) and C2–H ($\delta = 5.56$ for **12** and $\delta = 5.80$ for **13**) which were ascertained by selective decoupling measurements at C9–H. On the other hand, there was considerable difficulty in estimating the stereochemistry at C4 because of somewhat broadened multiplet peaks. In order to clarify the spin–spin coupling information between C4–H and C5–H, 2, 3-bis(methoxycarbonyl) derivatives **15** and **16** were prepared from dimethyl bicyclo[3.2.2]nona-6,8-diene-6,7-dicarboxylate (**14**)[9] under similar conditions (Scheme 3). As we would expect, simplified ^{1}H NMR spectrum was observed and the coupling constants between C4–H and C5–H for **15** and **16**

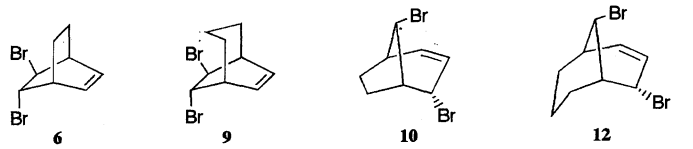


Scheme 3.

could be determined as $J = 6.4$ Hz and $J =$ ca. 0 Hz, respectively. The configuration at C4 was elucidated by analyses of Karplus angles between C4–H and C5–H (30° for **15** and 85° for **16**) using a ball and stick model. This model inferred the *endo*-configuration of **15** and *exo*-configuration of **16** for respective C4–Br atoms. Fortunately, X-ray structural analysis for a single crystal of **16** could be performed and *exo*-configuration for C4–Br was confirmed.[10] Thus the chemical shift of C4–H is assigned for **15** as $\delta = 5.52$ and for **16** as $\delta = 4.92$ and observed shift deviation by 0.60 ppm for C4–H between **15** and **16** is considered as anisotropic electric dipole deshielding by a polar C9–Br bond which aligned close to C4–H atom in the case of **15**.[11] Similar shift deviation is observed also by 0.68 ppm between C4–Hs of **12** and **13**. The structure of C4–Br for dibromide **12** is also estimated as *endo*-configuration by reference to described shift deviation.

Although the dibromide **13** was converted to **12** presumably via an allylic anion intermediate by heating with an equimolar amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene for 77 h in 33% yield, a thermal interconversion between the dibromides **12** and **13** was not observed under the conditions in reflux dichloromethane, in carbon tetrachloride, nor in xylene for 4 h from the two sides. The product distribution spectrum of the reaction of **4** in dichloromethane and in carbon tetrachloride at 0 °C was determined by ^{1}H NMR analysis as *cis*-**5** : *trans*-**5** : **10**=25 : 45 : 30 and 4 : 21 : 75, respectively. This distribution spectrum of **7** was also estimated by a similar method as **12** : **13**=50 : 50 in dichloromethane and 23 : 77 in carbon tetrachloride. At present the reason of this solvent effect is not so clear.

In spite of careful analyses of each reaction mixture, we could not find 1,2-addition products such as **6** and **9** which were reported as the products for the similar reactions. Similarities of ^{1}H NMR (60 MHz) data between previously reported as **6** and here proposed **10** confirm that the structure of the dibromide from bicyclodiene **4** is not 1,2-addition product **6** but skeleton rearranged dibromide **10**. The other already reported dibromide **9** also can be presumed to be rearranged structure **12** by comparison of 60 MHz ^{1}H NMR data (Fig. 1). On proposed mechanism for the present re-

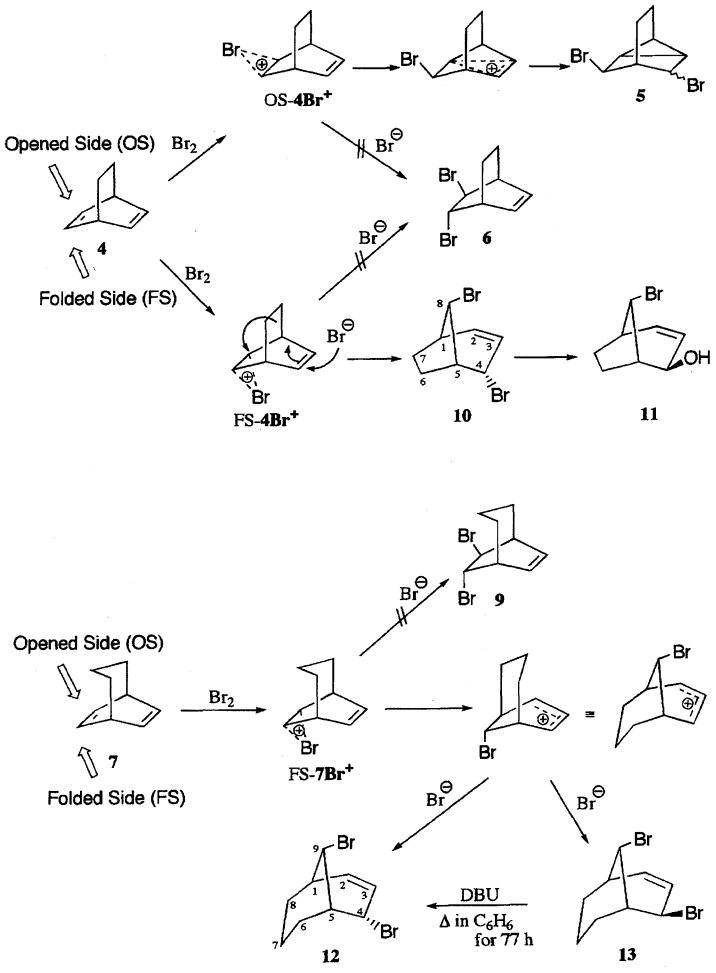


6	9	10	12
4.17 (m, 1H)	1.15 - 1.95 (m, 5H)	1.75 - 1.90 (m, 3H)	1.25 - 1.95 (m, 5H)
5.25 - 5.80 (m, 3H)	2.42 (m, 2H)	2.30 - 2.55 (m, 3H)	2.25 - 2.90 (m, 3H)
	2.72 (m, 1H)	4.08 (m, 1H)	4.40 (br s, 1H)
Other protons	4.47 (m, 1H)	5.23 (m, 1H)	5.20 (br d, 1H)
were not reported.	5.25 (br d, 1H)	5.53 - 5.67 (m, 2H)	5.35 - 5.70 (m, 1H)
	5.35 - 5.74 (m, 1H)		6.10 (dd, 1H)
	6.09 (q, 1H)		

Fig. 1. ^{1}H NMR (60 MHz) data for previously reported **6** and **9** and for here proposed **10** and **12** in CCl_4 (δ).

sults is illustrated in Scheme 4. While the term of *endo-* or *exo-* should be used for a correct definition for the attacking direction of the bromine, in this paper, it is convenient to define a folded side (FS) and a opened side (OS) on the basis of common folded 1,4-cyclohexadiene part as mentioned in Scheme 4. The legal definition *endo-* or *exo-* is somewhat complicated for the following discussion, because the folded side (FS) defined here corresponds to an *endo*-side for diene **4** and to an *exo*-side for diene **7**.

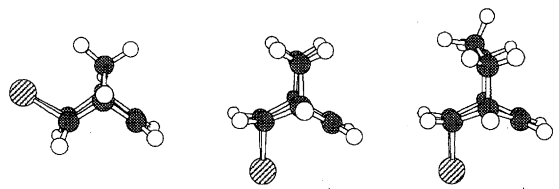
Formation of 1,5-addition products such as *cis-* and *trans-***5** is due to an OS attack of bromine to bicyclodiene **4** by analogy to the reaction products from a norbornadiene **1** such as *cis-* and *trans-***2**, although the dibromide corresponding to **3** is not formed in the present conditions. The stereochemistry of another type of a skeleton rearranged dibromide **10** is presumed to be due to an opposite (FS) attack of bromine to the bicyclodiene **4**. That is to say, an OS attack leads to the 1,5-addition products *cis-* and *trans-***5** via OS-bromonium ion (OS-**4Br**$^+$) and a FS attack of bromine leads to a new type of skeleton rearranged dibromide by concerted OS attack of bromide ion to the FS-bromonium ion (FS-**4Br**$^+$) and 1,2-migration of the methylene bridge. On the other hand, the bicyclodiene **7** gives no 1,5-addition products but gives a pair of rearranged dibromides, **12** and **13**. While



Scheme 4.

Fickes et al. reported that the 1,5-addition product **8**, which is presumed to be an OS attacked product, comprised 10% of the products,[5] we could not find out it, but we found simultaneously formed **12** and **13** and unreacted **7**, despite a precise ^{1}H NMR monitoring of the reaction mixture in the course of the reaction. This means the addition of bromine only occurred from a FS direction under our conditions to give an allyl cation by 1,2-migration of the trimethylene-bridge of an FS-bromonium cation (FS-**7Br**$^+$). Because no interconversion between the dibromides **12** and **13** could be observed under the reaction conditions, subsequent bromide ion addition occurs competitively from both upper and lower directions of the allyl cation plane. Thus obtained dibromides explain that the side of bromine attack to the bicyclodiene **7** is on opposite side in the case of norbornadiene, while the bicyclodiene **4** displays an intermediary character between norbornadiene and bicyclodiene **7** for the reaction.

The differences between thermodynamic stability of OS- and FS-bromonium cations were estimated by comparison of calculated heats of formations (H_f) for tentative bromonium ion structures of norbornadiene, **4**, and **7** by means of MNDO calculation. The difference between the H_f values of OS- and FS-bromonium ions (ΔH_f) and optimized interatomic distances are shown in Fig. 2, along with ball and stick structure of MNDO predicted more stable isomer in each case. An ab initio MO optimized structure of three-membered ring for bromonium ion of ethylene was reported as C–C : 1.44 Å and C–Br : 2.17 Å.[12] This calculation suggests that there is a significant difference with regard to a stability of bromonium ion between **1** and its homologs **4** and **7**. Although, the FS-**1Br**$^+$ is less stable compared to the OS-**1Br**$^+$ by 1.1 kcal mol^{-1}, the FS-**4Br**$^+$ and FS-**7Br**$^+$ are more stable form than *exo*-forms by 1.5 and 4.0 kcal mol^{-1}, respectively. The difference between the stability of bromonium ions of norbornadiene and its homologs may contribute to formation of an entirely different dibromide. That is to say, FS-bromonium ion of the bicyclodiene gives skeleton rearrangement products rather than homo-conjugated addition products because of predominant migration of methylene-bridge toward the three-membered ring of bromonium ion. There may be a tendency that the more stable the *endo*-bromonium ion becomes, the more the skeleton rearrangement becomes remarkably. For a further clarification of this point, the reaction of a bicyclo[4.2.2]deca-7,9-diene, whose first straightforward synthesis was reported recently, is under investigation.



	OS-**1Br**$^+$	FS-**4Br**$^+$	FS-**7Br**$^+$
ΔH_f (kcal/mol)	1.08	1.51	3.93
$D_{C\text{-}C}$(Å)	1.500	1.493	1.489
$D_{C\text{-}Br}$(Å)	2.023	2.034	2.030

Fig. 2. MNDO optimized structure for bromonium ion of bicyclodiene **1**, **4**, and **7**; The ΔH_f values and interatomic distances of trigonal bromonium ion moiety (D_{C-C},D_{C-Br}) are also designated.

Experimental

Melting points were determined with a Yanagimoto micromelting point apparatus and were uncorrected. Silica gel HF_{254} (Merck) for thin-layer chromatography and silica gel Woelm 32-63 for preparative MPLC were used. IR spectra were recorded on a JASCO FT-IR 5000 spectrophotometer. ^{1}H and ^{13}C NMR were measured on a Varian XL-200 or XL-500 spectrometer. Electronic Spectra were recorded on a Hitachi 288 spectrophotometer. Mass spectrometry was performed on a JEOL JMS-DX300 mass spectrometer coupled to JMA-3100 data analysis system. Elemental analyses were performed on a Yanagimoto MT-2 CHN-corder. The molecular orbital (MNDO) calculation was carried out on a NEC ACOS-2000 computer of Okayama University Computer Center.

General Procedure for Bromination of Bicyclodienes 4,7, and 14. A standard bromine solution was made by direct weighing using a glass-capillary, followed by dilution with dichloromethane in a volumetric flask. To a solution of bicyclodiene in dichloromethane, an equimolar amount of the bromine standard solution was added dropwise through a dropping funnel at 0 °C under a nitrogen atmosphere, allowing the solution to decolorize between each drop. When the brown color persisted, the excess bromine was quenched with 10% sodium thiosulfate. The reaction mixture was diluted with dichloromethane, washed with saturated aqueous $NaHCO_3$ and brine, and then dried.

Bromination of Bicyclo[2.2.2]octa-2,5-diene. (4). A dried solution starting from bicyclodiene **4** (224 mg, 2.11 mmol) described in general procedure was evaporated in vacuo at room temperature and the residue was chromatographed on silica gel by MPLC with hexane as an eluent. Dibromides *trans*-**5** (180 mg, 32%) and **10** (112 mg, 20%) were obtained from hexane eluents. Further elution using ethyl acetate : hexane=2 : 8 (v/v) gave an allyl alcohol **11** (17 mg, 3%). A ^{1}H NMR spectrum of the reaction mixture before chromatographic operation indicated a formation of the dibromides *cis*-**5**, *trans*-**5**, and **10**. Although *cis*-**5** could not be isolated under the chromatographic conditions, the formation of it was confirmed by a characteristic multiplet signal at $\delta = 4.6$ for *ipso*-protons[4] of bromine.

(6*SR*,8*SR*)-6,8-Dibromotricyclo[3.2.1.0^{2,7}]octane (*trans*-5): Colorless oil; IR (neat) 3052 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.27$ (1H, dt, $J = 7.9$ and 2.6 Hz), 1.63 (1H, m), 1.73 (1H, m), 2.00 (2H, m), 2.07 (1H, ddd, $J = 13.9$, 5.2, and 2.2 Hz), 2.17 (1H, m), 2.38 (1H, m), 4.42 (1H, s), 4.94 (1H, dt, $J = 4.7$ and 1.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 14.1$ (t), 21.3 (d), 24.5 (d), 25.5 (t), 30.1 (d), 44.6 (d), 53.9 (d), 55.8 (d). Found: C, 35.88; H, 3.90%. Calcd for $C_8H_{10}Br_2$: C, 36.13; H, 3.79%.

(1*RS*,4*SR*,5*RS*,8*SR*)-4,8-Dibromobicyclo[3.2.1]oct-2-ene (10): Colorless oil; IR (neat) 1634 cm^{-1} (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.90$ (3H, m), 2.39 (1H, m), 2.59 (1H, m), 2.63 (1H, m), 4.19 (1H, ddd, $J = 5.3$, 3.7, and 1.6 Hz), 5.37 (1H, m), 5.67 (1H, dtd, $J = 9.7$, 1.9, and 0.6 Hz), 5.78 (1H, ddd, $J = 9.7$, 6.2, and 1.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 24.6$ (t), 31.5 (t), 40.5 (d), 45.3 (d), 54.1 (d), 57.1 (d), 126.8 (d), 132.3 (d). Found: C, 36.26; H, 3.70%. Calcd for $C_8H_{10}Br_2$: C, 36.13; H, 3.79%.

(1*RS*,4*RS*,5*SR*,8*SR*)-8-Bromo-4-hydroxybicyclo[3.2.1]oct-2-ene (11): Colorless oil; IR (neat) 3562 (OH) and 1640 cm^{-1} (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.29$ (1H, ddd, $J = 13.7$,

9.7, and 6.8 Hz), 1.66 (2H, m), 1.87 (1H, m), 2.63 (1H, m), 2.70 (1H, m), 2.90 (1H, d, J = 11.8 Hz), 3.74 (1H, br d, J = 11.8 Hz), 4.12 (1H, ddd, J = 4.8, 3.6, and 1.3 Hz), 5.79 (1H, dtd, J = 9.6, 3.7, and 1.7 Hz), 5.91 (1H, dtd, J = 9.6, 6.6, and 1.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 25.2 (t), 28.9 (t), 41.1 (d), 43.2 (d), 50.2 (d), 73.2 (d), 126.8 (d), 131.5 (d). Found: C, 47.55; H, 5.31%. Calcd for $C_8H_{11}BrO$: C, 47.32; H, 5.46%.

Bromination of Bicyclo[3.2.2]nona-6,8-diene (7). Bicyclodiene **7** (182 mg, 1.51 mmol) was brominated using an equimolar amount of bromine standard solution, as described in the general procedure. The thus obtained reaction mixture was chromatographed (ethyl acetate : hexane=5 : 95, v/v) on silica gel by MPLC to give dibromides **12** (170 mg, 40%) and **13** (165 mg, 39%).

(1*RS*, 4*SR*, 5*RS*, 9*SR*)- 4, 9- Dibromobicyclo[3.3.1]non- 2- ene (12): Colorless prisms (mp 28—29 °C); IR (neat) 1630 cm^{-1} (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.43 (1H, m), 1.65 (3H, m), 1.78 (1H, m), 2.43 (1H, br s), 2.45 (1H, m), 2.72 (1H, br s), 4.49 (1H, m), 5.27 (1H, m), 5.56 (1H, dddd, J = 10.1, 5.8, 1.8, and 1.8 Hz), 6.08 (1H, ddd, J = 10.1, 2.6, and 0.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 15.7 (t), 30.6 (t), 32.48 (t), 38.65 (d), 40.93 (d), 52.13 (d), 57.0 (d), 128.5 (d), 131.3 (d). Found: C, 38.35; H, 4.18%. Calcd for $C_9H_{12}Br_2$: C, 38.61; H, 4.32%.

(1*RS*, 4*RS*, 5*RS*, 9*SR*)- 4, 9- Dibromobicyclo[3.3.1]non- 2- ene (13): Colorless prisms (mp 79—80 °C); IR (KBr) 1625 cm^{-1} (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.32 (1H, m), 1.38 (1H, m), 1.63 (3H, m), 1.85 (1H, m), 2.87 (1H, m), 2.91 (1H, m), 4.41 (1H, ddd, J = 2.6, 1.4, and 1.4 Hz), 4.59 (1H, dd, J = 3.6 and 1.7 Hz), 5.80 (1H, dddd, J = 10.1, 6.1, 1.6, and 1.6 Hz), 6.21 (1H, ddd, J = 10.1, 3.6, and 1.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 15.5 (t), 30.1 (t), 34.3 (t), 38.4 (d), 43.8 (d), 46.5 (d), 50.2 (d), 129.2 (d), 130.8 (d). Found: C, 38.40; H, 4.21%. Calcd for $C_9H_{12}Br_2$: C, 38.61; H, 4.32%.

Isomerization of Dibromide 13 to Dibromide 12. A dry benzene (10 ml) solution of dibromide **13** (56 mg, 0.2 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 61 mg, 0.4 mmol) was heated to reflux for 77 h under a nitrogen atmosphere. Benzene was removed in vacuo and the residue was chromatographed (ethyl acetate : hexane=10 : 90 v/v) on silica gel by MPLC to give isomerized dibromide **12** (17 mg, 31%) and unreacted starting dibromide **13** (4 mg).

Bromination of Dimethyl Bicyclo[3.2.2]nona-6,8-diene-6,7-dicarboxylate (14). To a dichloromethane solution of a bicyclodiene **14** (131 mg, 0.554 mmol), an equimolar amount of the bromine standard solution was added in the manner described in the general procedure. A residue from the reaction mixture was chromatographed (ethyl acetate : hexane=5 : 95 v/v) on silica gel by MPLC to give dibromides **15** (90 mg, 23%) and **16** (119 mg, 30%).

Dimethyl (1*RS*,4*SR*,5*RS*,9*SR*)-4,9-Dibromobicyclo[3.3.1]non-2-ene-2,3-dicarboxylate (15): Colorless prisms (mp 110—118 °C); IR (KBr) 1738, 1719 (C=O), 1640 cm^{-1} (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.55 (2H, m), 1.69 (1H, m), 1.88 (1H, m), 2.11 (1H, dq, J = 13.8 and 3.0 Hz), 2.46 (1H, dq. J = 13.8 and 3.0 Hz), 2.57 (1H, m), 3.12 (1H, m), 3.76 (3H, s), 3.85 (3H, s), 4.50 (1H, t, J = 3.0 Hz), 5.52 (1H, d, J = 6.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 15.2 (t), 30.1 (t), 32.7 (t), 40.4 (d), 40.7 (d), 50.0 (d), 52.4 (q), 52.5 (q), 54.2 (d), 132.4 (s), 140.6 (s), 166.0 (s), 166.9 (s). Found: C, 39.13; H, 4.01%. Calcd for $C_{13}H_{16}Br_2O_4$: C, 39.42; H, 4.07%.

Dimethyl (1*RS*,4*RS*,5*RS*,9*SR*)-4,9-Dibromobicyclo[3.3.1]non-2-ene-2,3-dicarboxylate (16): Colorless prisms (mp 74—75 °C); IR (KBr) 1740, 1719 (C=O), 1638 cm^{-1} (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.28 (1H, m), 1.47 (1H, m), 1.70 (3H, m), 1.97 (1H, m), 3.03 (1H, m), 3.44 (1H, m), 3.80 (3H, s), 3.85 (3H, s), 4.45 (1H, t, J = 2.7 Hz), 4.92 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 15.4 (t), 29.8 (t), 34.1 (t), 40.4 (d), 43.5 (d), 43.7 (d), 47.5 (d), 52.6 (q), 52.7 (q), 134.7 (s), 138.5 (s), 166.5 (s), 166.8 (s). Found: C, 39.25; H, 3.99%. Calcd for $C_{13}H_{16}Br_2O_4$: C, 39.42; H, 4.07%.

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