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Unprecedented anomalous stereochemistry of halogen additions to *syn*- and *anti*-9,9′-bibenzonorbornenylidenes

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Abstract

Exclusive *syn*(*cis*)-addition of Br_2 to *syn*-9,9′-bibenzonorbornenylidene (**1**) took place to give the corresponding *vic*-dibromide (**3**) quantitatively with retention of the configuration of **1**. Meanwhile, *anti*(*trans*)-addition of Br_2 to *anti*-9,9′-bibenzonorbornenylidene (**2**) also occurred furnishing the same dibromide **3** quantitatively with inversion of the configuration of **2**.

Keywords: halogen addition; 9,9′-bibenzonorbornenylidenes; *syn*-addition; *anti*-addition.

Much attention has been paid to halogen addition to sterically congested alkenes since the first isolation of epibromonium tribromide by reaction of 2,2′-biadamantylidene with Br_2.[1] When the benzonorbornenylidene group constitutes the double bond which participates in the reaction, it may exert not only steric effects due to its bulkiness but also electronic effects by neighboring group participation.[2,3] In addition, investigation with a pair of *syn*- and *anti*-alkene isomers, which carries this group, would reveal the stereochemical course of many reactions. Keeping these facts in mind, quite recently, we have synthesized the sterically congested alkenes *syn*-9,9′-bibenzonorbornenylidene (**1**) and *anti*-9,9′-bibenzonorbornenylidene (**2**).[4] We report here the unprecedented anomalous stereochemistry of halogen addition to **1** and **2**.

The results of reactions of Br_2, ICl, and Cl_2 with **1** and **2** are summarized in Table 1. Addition of a solution of 1 equiv. of Br_2 in CH_2Cl_2 to a solution of the *syn*-alkene **1** in the same solvent at −78°C resulted in the immediate disappearance of the bromine color and furnished the adduct quantitatively (entry 1). The structure of the adduct was unambiguously determined to be the

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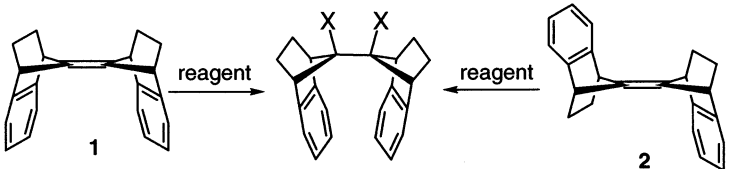
Table 1
Reactions of **1** and **2** with Br_2, ICl and Cl_2 in CH_2Cl_2

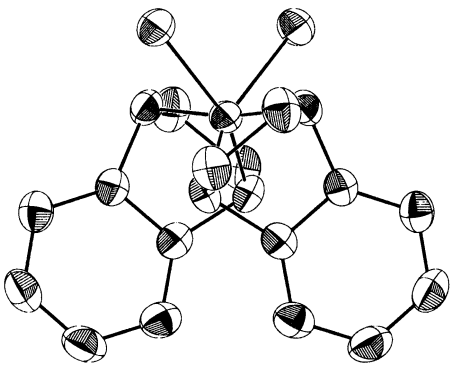


3: X = Br
8: X = Cl

Entries	Alkenes	Reagent	Temp. (°C)	Products (yield, %)			Entries	Alkenes	Reagent	Temp. (°C)	Products (yield, %)		
				Dihalides	**1**	**2**					Dihalides	**1**	**2**
1	**1**	Br_2	−78	**3**; 100[a]			10	**1**	ICl	−40	**8**; 50[b]	30[b]	20[b]
2	**2**	Br_2	−78	**3**; 100[a]			11	**2**	ICl	−78	**8**; 50[b]	30[b]	20[b]
3	**1**	Br_2	18	**3**; 100[a]			12	**1**	2ICl	−40	**8**; 100[a]		
4	**2**	Br_2	18	**3**; 100[a]			13	**2**	2ICl	−78	**8**; 100[a]		
5	**1**	0.5 Br_2	−78	**3**; 50[b]	50[b]		14	**1**	Cl_2[c]	18	**8**; 100[a]		
6	**2**	0.5 Br_2	−78	**3**; 50[b]		50[b]	15	**2**	Cl_2[c]	18	**8**; 85[a], **11**; 15[a]		
7	**1**	0.5 Br_2	18	**3**; 50[b]	45[b]	5[b]							
8	**2**	0.5 Br_2	18	**3**; 50[b]	13[b]	37[b]							
9	**1**+**2** (0.5:0.5)	0.5 Br_2	−78	**3**; 50[b]	34[b]	16[b]							

[a] Isolated yield.
[b] Yields determined by ^1H NMR.
[c] Cl_2 was used in excess.

dibromide (**3**) by X-ray diffraction analysis (Fig. 1).[5] The two bromine atoms in **3** are twisted with a torsion angle of 72°, thus adopting a *gauche* conformation. The ^{1}H and ^{13}C NMR spectrum analyses showed that the *gauche* conformation is also retained in solutions.[6] The above results demonstrate that: (1) the bromine addition proceeded by *syn*(*cis*)-addition, in marked contrast to common bromine additions,[7] with *retention of the configuration* of **1**, and (2) the addition took place at the more sterically crowded ethylene bridge side. More surprisingly, the bromine addition to the *anti*-alkene **2** under the same conditions, which also took place very rapidly, provided the same dibromide **3** quantitatively, demonstrating that the bromine addition now proceeded by *anti*(*trans*)-addition with *inversion of the configuration* of **2**.



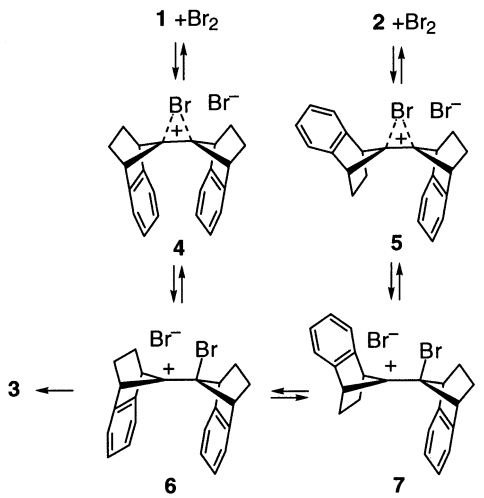


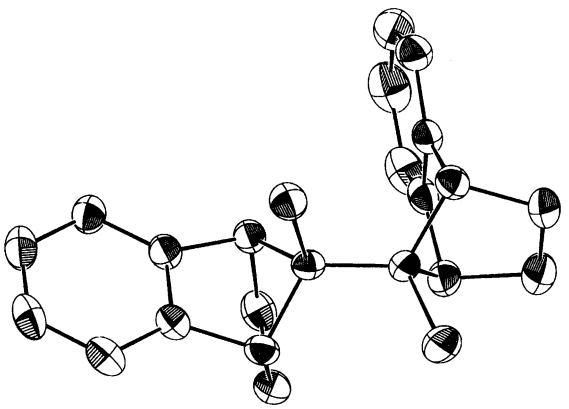
Figure 1. Molecular structure of **3**

Elevating of the reaction temperature to 18°C did not change the stereochemistry of the addition (entries 3 and 4). Reactions of **1** and **2** with 0.5 equiv. of Br_2 at −78°C gave the dibromide **3** in 50% yield; the configuration of the recovered **1** and **2** remained unchanged (entries 5 and 6). However, the reactions at 18°C resulted in the *syn–anti* isomerization of the recovered alkenes, with formation of **3** in 50% yield (entries 7 and 8). A competitive reaction showed that the bromine addition to **2** is faster than that to **1** (entry 9).

The following can best accommodate the experimental observations. Br_2 approaches the double bond of **1** from the ethylene chain side to give the epibromonium ion intermediate (**4**), which is doubly stabilized by neighboring group participation of both benzene rings.[3] On the other side, the epibromonium ion intermediate (**5**), formed from **2** and bromine, undergoes internal rotation about the C–C bond more quickly than the addition of Br^-, through concomitant ring-opening of the epibromonium ion structure, to give the more stable conformer **4**. Approach of the nucleophile Br^- from the back-side of **4** is disfavored by two factors: (1) neighboring group participation of the benzene rings, and (2) steric hindrance by two benzene rings which became much closer compared to those in **1**. Thus, the addition of Br^- at the front-side, probably via ring-opening carbenium ion formation (**6**), results in the exclusive formation of **3**. The observed isomerization of **1** and **2**, by use of 0.5 equiv. of Br_2, indicates that the formation of both **4** and **5** is reversible at 18°C.

The reactions of **1** and **2** with ICl provide further unprecedented features of the reaction. The reaction of **1** with 1 equiv. of ICl in CH_2Cl_2 at −40°C provided the dichloride (**8**) in 50% yield together with **1** (30%) and the isomerized alkene **2** (20%) (entry 10). The expected ICl adduct was not formed. The same products were also formed in the same ratio by reaction of **2** with ICl (entry 11). The reactions of **1** and **3** with 2 equiv. of ICl furnished **8** quantitatively (entries 12 and 13). In all of these reactions, I_2 was liberated as characterized from its color. Separate experiments showed that I_2 did not add to **1** and **2** even at room temperature and also did not bring about isomerization of **1** and **2**. The following deductions made from these observations: (1) addition of I^+ to **1** and **2** is reversible, (2) I^- is expelled from the initial adduct (**9**) to produce the carbocation intermediate (**10**)[8] with relief from steric strain,[2] and (3) addition of the nucleophile (Cl^-) to **10** furnishes the final product **8**.

The reaction of **1** with Cl_2 also gave **8** quantitatively, whereas the reaction of **2** with Cl_2 produced the adduct **11** in 15% yield, in addition to **8** in 85% yield. The structure of **11** was determined by X-ray diffraction analysis (Fig. 2).[9] These results reveal that the addition of Cl^- to the initial intermediate (**12**), formed from **2**, becomes competitive with the internal rotation to **10** because Cl^- is a smaller and better nucleophile than Br^- in the aprotic solvent CH_2Cl_2.



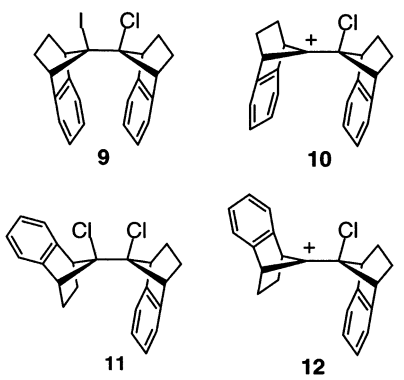


Figure 2. Molecular structure of **11**

Acknowledgements

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5. Crystal data for **3**: orthorhombic, *Pbna*, $a=8.2680(4)$, $b=13.119(1)$, $c=16.197(1)$ Å, $V=1756.8(2)$ Å^3, $Z=4$, $T=295$ K, $R=0.045$, $wR=0.047$, GOF = 2.159.
6. Free rotation about the central C–C bond does not occur because of steric hindrance. Thus, in the ^{1}H NMR spectrum, one of the two bridgehead hydrogens appears at δ 1.57, while the other appears at δ 4.07, because of the ring current effect of the benzene ring, and in the ^{13}C NMR spectrum, three sp^3 and six aromatic carbon peaks are observed over the temperature range 25–60°C. The same holds for the dichloride **8**.
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8. The remaining ICl would act as a Lewis catalyst for removal of I^-.[10] Treatment of the dibromide **3** with ICl also produces **8** quantitatively.
9. Crystal data for **11**: triclinic, $P\bar{1}$ $a=7.423(1)$, $b=8.429(1)$, $c=13.972(2)$ Å, $\alpha=104.012$, $\beta=93.364(6)$, $\gamma=96.141(6)°$, $V=840.1(2)$ Å^3, $Z=2$, $T=295$ K, $R=0.046$, $wR=0.049$, GOF = 1.154.
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