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Synthesis and Structure of Sterically Congested, New Alkenes, *syn*- and *anti*-9,9′-Bibenzonorbornenylidenes

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Sterically congested alkenes, *syn*- and *anti*-9,9′-bibenzonorbornenylidenes (**1a**) and (**1b**), were synthesized starting from 9-benzonorbornenone in good overall yields and were isolated in pure form. Their structures were elucidated by analyses of NMR spectra and established by X-ray crystallographic analysis. Structures of the two episulfides, which served as precursors leading to **1a** and **1b**, were also determined by X-ray crystallographic analysis.

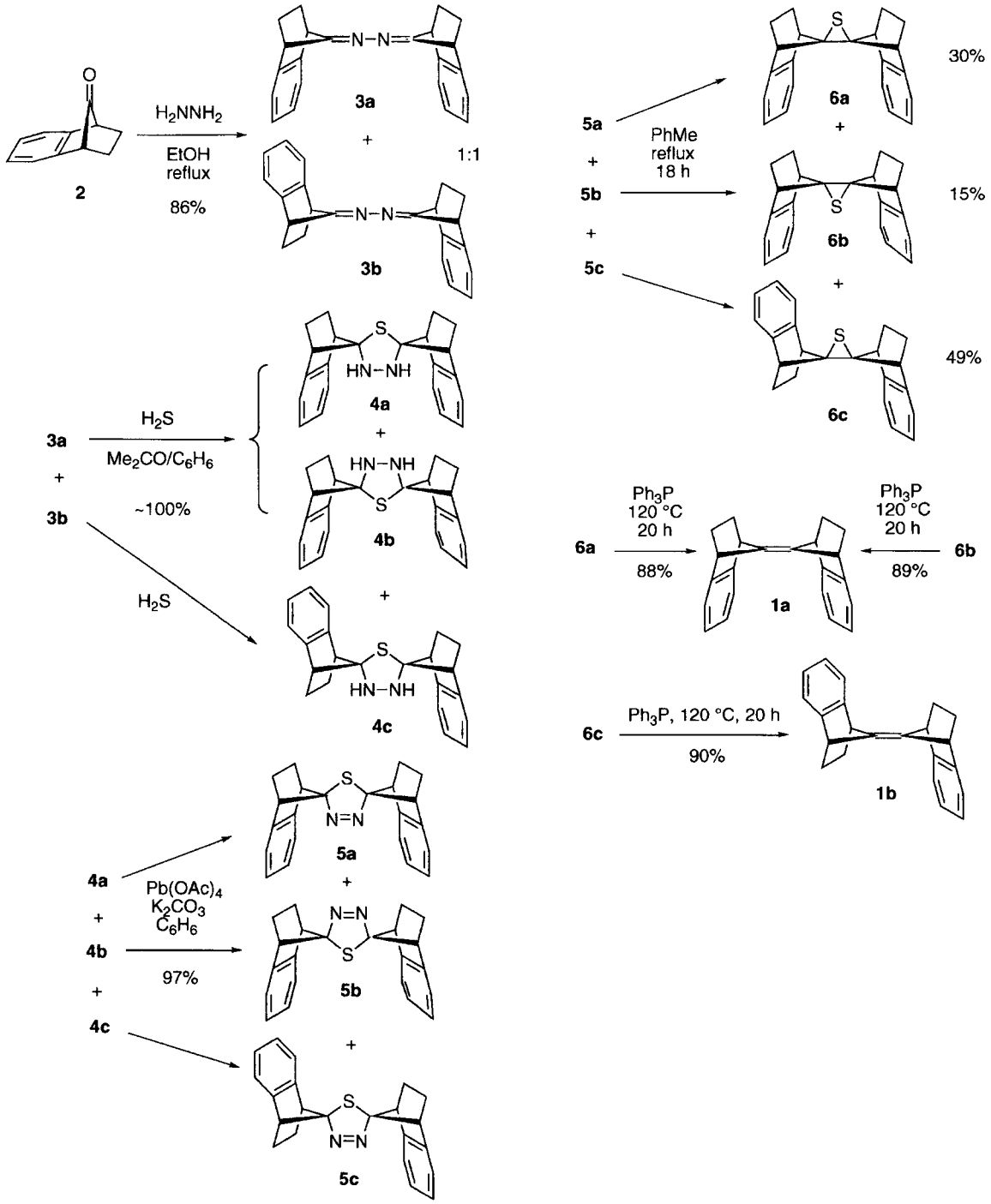
In our continuing study on the sulfuration of alkenes and alkynes by elemental sulfur and some other reagents,[1,2] we have designed 9,9′-bibenzonorbornenylidene (**1**), the dibenzo analog of 7,7′-binorbornylidene,[3,4] as one of the suitable substrates. Although syntheses, structures, and reactions of a great number of congested alkenes have been investigated in depth from a variety of viewpoint,[5] **1** still remains to be synthesized. The alkene **1** is of particular interest because, when the benzonorbonenylidene group constitutes the double bond concerned, it may exert not only steric effects by its bulkiness but also electronic effects by neighboring group participation.[6] In addition, satisfactory synthesis of *syn*- and *anti*-isomers of **1** allows a stereochemical study of not only sulfuration but also other many reactions. Herein we report the synthesis and X-ray crystallographic analysis of *syn*- and *anti*-9,9′-bibenzonorbornenylidenes (**1a**) and (**1b**).

Synthesis of Alkenes 1a and 1b. Isomeric alkenes **1a** and **1b** were prepared by Barton–Kellogg olefination starting from 9-benzonorbornenone (**2**)[7] in a good overall yield and in pure form (Scheme 1).[8,9] Thus, treatment of **2** with hydrazine monohydrate in refluxing EtOH gave a 1 : 1 isomeric mixture of azines (**3a**) and (**3b**) in 86% yield. Then, H_2S gas was bubbled into a mixture of **3a** and **3b**, dissolved in a mixed solvent of Me_2CO and C_6H_6, which produced a mixture of three isomeric thiadizolidines, (**4a**), (**4b**), and (**4c**), quantitatively in the ratio ca. 35 : 25 : 40. Immediately, without further purification, the mixture of **4a**—**c** was oxidized with $Pb(OAc)_4$ to furnish a mixture of three isomeric thiadiazolines, (**5a**), (**5b**), and (**5c**), in the ratio ca. 35 : 25 : 40 in 97% yield. The mixture of **5a**—**c** was then heated in refluxing toluene for 18 h, which provided a mixture of three isomeric episulfides, (**6a**), (**6b**), and (**6c**),with extrusion of N_2. Purification of the above isomeric mixture by silica-gel column chromatography allowed the isolation of **6a**, **6b**, and **6c** in pure form in 30, 15, and 49% isolated yields, respectively. Finally, desulfurization of the episulfides provided **1**. Thus, both **6a** and **6b** afforded the *syn*-alkene **1a**, with retention of the original stereochemistry, in 89 and 88% yields, respectively, when heated with Ph_3P without solvent at 120 °C for 20 h, while **6c** provided the *anti*-alkene **1b** in 90% yield under the same conditions.

Although the structures of episulfides **6a** and **6c** and alkenes **1a** and **1b** were established by X-ray crystallographic analyses, their structures are also predictable by analyses of NMR. The episulfide **6c** is easily differentiated from episulfides **6a** and **6b** by ^{13}C NMR spectra because the former isomer shows six sp^3 and six sp^2 carbon peaks, whereas the latters exhibit three sp^3 and three sp^2 carbon peaks. In addition, in the ^1H NMR, the two hydrogen atoms of the methylenes of **6c**, which face to the benzene ring and hence are placed under the influence of the ring current effect of the benzene ring,[10] appear as a multiplet centered at δ = 0.97, which is the highest field among the methylene hydrogen signals of the three episulfides. The same is true of the bridgehead hydrogen atoms of **6a**. The differentiation of **6a** and **6b** is also made by ^1H NMR analysis. The two benzene rings of **6a** are placed face to face, and hence their hydrogen atoms resonate at higher fields (δ = 6.64—6.76) than those of **6b** (δ = 7.10—7.13 and 7.18—7.21) by ring current effect of the benzene rings.

On the other hand, in the case of the alkenes **1a** and **1b**, both compounds show six carbon peaks (two sp^3 and four sp^2 carbon peaks). However, comparison of the ^1H NMR spectra easily allows the differentiation of these alkenes. The benzene ring hydrogen signals of the *syn*-alkene **1a** appear as two multiplets at δ = 6.96—6.99 and 7.06—7.09, which are higher than the corresponding signals of the *anti*-alkene **1b**, δ = 7.05—7.08 and 7.14—7.17, due to the ring current effect of the benzene rings. Meanwhile, the methylene hydrogens of **1b**, which face the benzene ring, appear as a multiplet at δ = 1.10—1.17, which is higher than the methylene hydrogen signals of **1a**, δ = 1.22—1.26 and 1.84—1.93.

Finally, it should be added that the separation of the stereoisomers at the episulfide stage is crucial for isolation of **1a** and **1b** in pure form. Although the conversion of **5** into **1** was made in one-pot without isolation of **6**, separation of **1a**



Scheme 1.

and **1b** at this stage was fruitless, despite many attempts.

X-Ray Crystallographic Analysis of Episulfides 6a and 6c and Alkenes 1a and 1b. Figures 1 and 3 show the molecular structures of the episulfides **6a** and **6c**, respectively. Selected bond length and bond angle data of **6a** and **6c** are summarized in Figs. 2 and 4, respectively. The C(1)–C(2) bond lengths of **6a**, 1.455(4) Å, and of **6c**, 1.464(3) Å, are slightly shorter than those of the common episulfides, 1.48 Å.[11] Meanwhile, the C–S bond lengths, 1.835(3) Å for **6a** and 1.822(3) and 1.829(3) Å for **6c**, are slightly longer than or nearly equal to those of the common episulfides, 1.82 Å. No particular deviation of the bond angles, compared with those of the common episulfides, is observed.

Figures 5 and 8 show the ORTEP drawings of the *syn*-alkene **1a** and the *anti*-alkene **1b**, respectively. Selected bond length and bond angle data of **1a** and **1b** are given in Figs. 6 and 9, respectively. Figures 7 and 10 show the CPK model structures of **1a** and **1b**, respectively. For **1a**, the dihedral angle of C(3)–C(1)–C(2)–C(5) and that of C(4)–C(1)–C(2)–C(6) are as small as 2.1(2)° and 1.3(2)°, respectively, and, also for **1b**, the dihedral angle of C(3)–C(1)–C(2)–C(5) and that of C(4)–C(1)–C(2)–C(6) are as small as 4.2(2)°

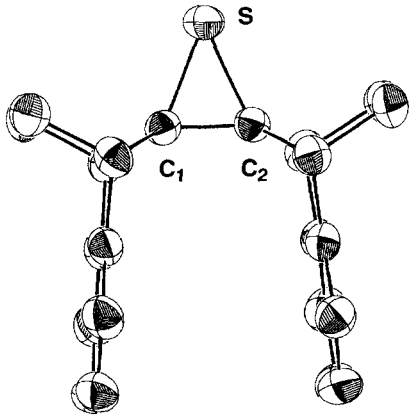


Fig. 1. ORTEP drawing of **6a**.

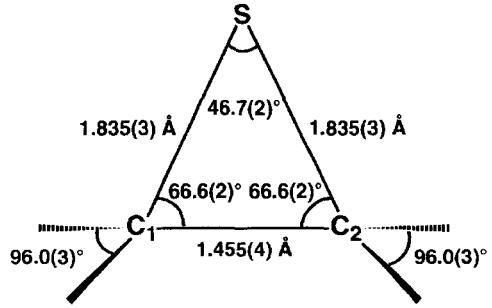


Fig. 2. Selected bond angles and bond lengths of **6a**.

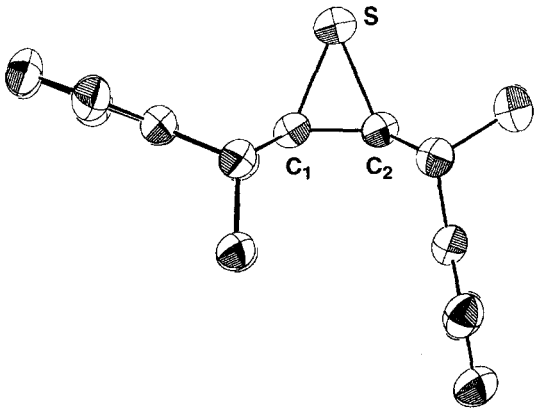


Fig. 3. ORTEP drawing of **6c**.

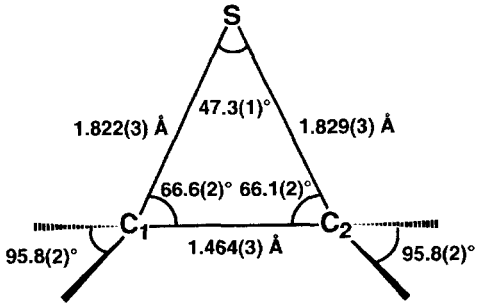


Fig. 4. Selected bond angles and bond lengths of **6c**.

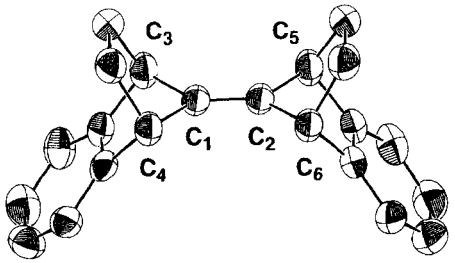


Fig. 5. ORTEP drawing of **1a**.

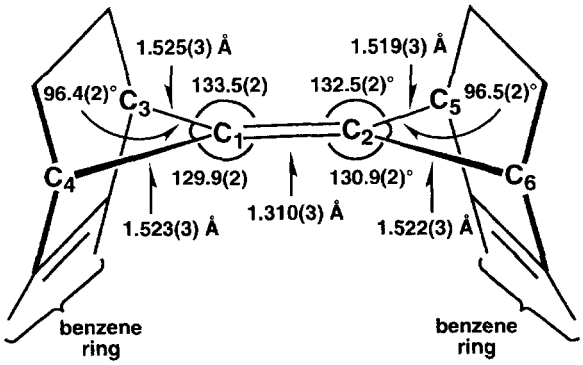


Fig. 6. Selected bond angles and bond lengths of **1a**.

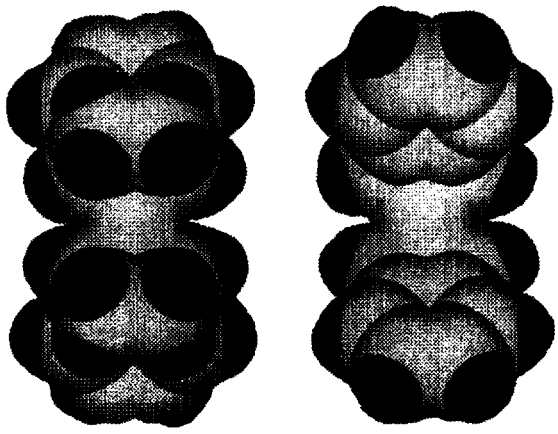


Fig. 7. CPK model structure of **1a** (right: a view from benzene ring side, left: a view from methylene side).

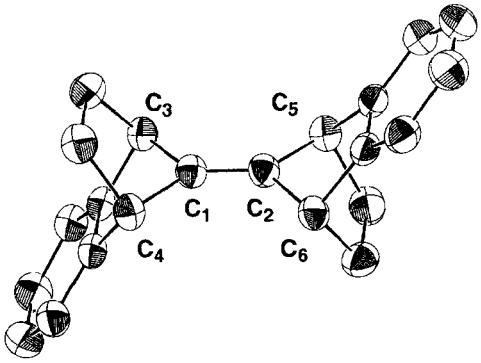


Fig. 8. ORTEP drawing of **1b**.

and 2.3(2)°, respectively. Thus, the double bond part of **1a** and **1b** is nearly planar. The bond length and bond angle data also show that no large geometrical differences exist between the right hand part and the left hand part of the two compounds. Thus, **1a** possesses a plane of symmetry (σ) and **1b** has a C_2 axis. The sole large difference in geometry,

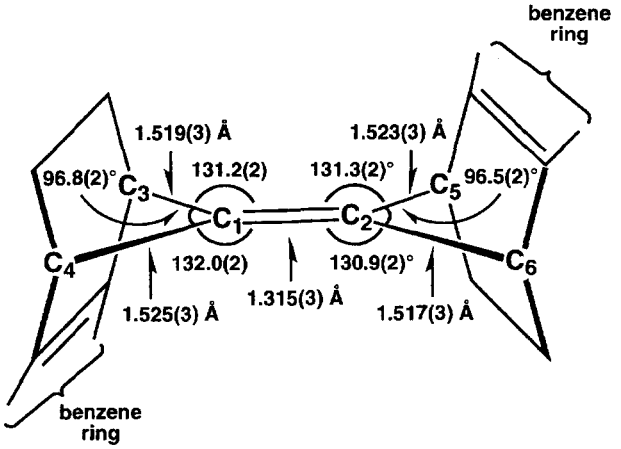


Fig. 9. Selected bond angles and bond lengths of **1b**.

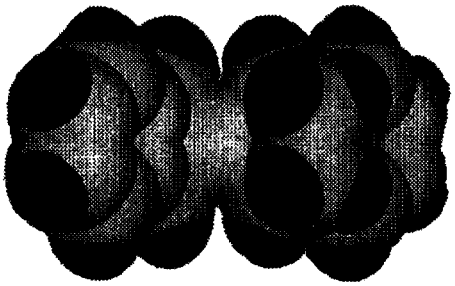


Fig. 10. CPK model structure of **1b**.

compared with the common alkenes,[12] is reduction of the C3–C1–C4 and C5–C2–C6 bond angles to ca. 96—97° with expansion of the other bond angles around C1 and C2 to ca. 130—134°. Finally, it should be stressed that the ORTEP drawings, Figs. 5 and 8, and the CPK model structures, Figs. 7 and 10, show that the double bonds of these two alkenes are surrounded by rigid σ- and π- frameworks, which would exert strong influences on the reactivities and stereochemical course of the reactions of these compounds.

Experimental

Solvents were purified and dried in the usual manner. All the reactions were carried out under argon. Silica-gel column chromatography was performed on silica gel 7734 (Merck, 70—230 mesh). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400, a Bruker AM400, a Bruker AM300, or a Bruker AC200 spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard. IR spectra were recorded on a Hitachi 270-50 spectrophotometer. Mass spectra were recorded on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

Preparation of a 1 : 1 Isomeric Mixture of Azines (3a) and (3b): A solution of $H_2NNH_2 \cdot H_2O$ (1.57 g, 31 mmol) in EtOH (7 ml) was added slowly to a solution of 9-benzonorbornenone (**2**) (9.01 g, 57 mmol) in EtOH (50 ml) under reflux. The resulting crystalline solid was collected by filtration, washed with a small amount of EtOH, and recrystallized from hexane to give 7.70 g (86%) of a 1 : 1 mixture of the two isomeric azines, **3a** and **3b**, of 9-benzonorbornenone: Colorless crystals; mp 251—252 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.21—1.41 (m, 4H), 1.96—2.03 (m, 0.5×2H), 2.07—2.17 (m, 0.5×6H), 3.62 (d, J = 3.7 Hz, 0.5×4H), 4.09 (d, J = 3.7 Hz, 0.5×2H), 4.19 (d, J = 3.7 Hz, 0.5×2H), 7.08—7.18 (m, 0.5×10H), 7.19—7.25 (m, 0.5×6H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 24.6, 25.1, 25.2, 40.7, 40.9, 45.5, 120.7, 120.8, 121.1, 121.2, 126.38, 126.40, 126.42, 126.5, 143.2, 143.5, 144.34, 144.37, 178.3, 178.7; IR (KBr) 2980, 2952, 2872, 1704, 1462, 1130, 1106, 760, 722, 504, 472 cm^{-1}. Found: C, 84.64; H, 6.45%. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45%.

Preparation of Isomeric Thiadiazolidines (4a—c): Into a suspension of a 1 : 1 mixture of azines **3a** and **3b** (8.36 g, 26.7 mmol), dissolved in a mixed solvent of acetone (50 ml) and C_6H_6 (150 ml), was bubbled H_2S gas at room temperature. After bubbling for 2 h, the mixture was evaporated under reduced pressure to give 9.37 g (100%) of a mixture of three isomeric thiadiazolidines **4a—c** in the ratio ca. 35 : 25 : 40 as a faint yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.15—1.19 (m, 4H), 1.35—1.40 [m, (0.25×2H)+(0.4×1H)], 1.44—1.49 [m, (0.25×2H)+(0.4×1H)], 1.96—2.03 [m, (0.35×4H)+(0.4×2H)], 2.13—2.17 [m, (0.25×4H)+(0.40×2H)], 3.11 [s, (0.25×4H)+(0.4×2H)], 3.26 [s, (0.4×2H)+(0.35×4H)], 7.08—7.22 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 25.8, 25.9, 26.8, 27.0, 52.2, 52.8, 52.9, 53.4, 103.1, 103.4, 104.1, 120.8, 121.0, 121.1, 121.2, 125.85, 125.89, 126.1, 145.7, 145.8, 146.6, 146.7; IR (KBr) 3316, 2976, 2944, 2868, 1784, 1692, 1582, 1470, 1276, 1166, 1024, 1016, 954, 938, 756, 590, 508 cm^{-1}.

Preparation of Isomeric Thiadiazolines (5a—c): A solution of a mixture of three isomeric thiadiazolidines **4a—c** (8.99 g, 26.0 mmol) in C_6H_6 (200 ml) was added dropwise over a period of 30 min to a suspension of $Pb(OAc)_4$ (15.0 g, 33.8 mmol) and K_2CO_3 (20.0 g, 145 mmol) in C_6H_6 (200 ml) under cooling by an ice bath. The mixture was then warmed slowly to room temperature and the reaction was quenched by addition of H_2O. The resulting precipitates were removed by filtration. The filtrate was washed with brine and then H_2O, dried over $MgSO_4$, and evaporated to give 8.68 g (97%) of a mixture of three isomeric thiadiazolines **5a—c**: colorless solid; mp 175—180 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.38—1.50 (m, 4H), 1.95—2.20 [m, (0.35×2H)+(0.4×4H)], 2.65—2.75 [m, (0.25×2H)+(0.4×2H)], 3.24 [s, (0.35×4H)+(0.4×2H)], 3.43 [s, (0.25×4H)+(0.4×2H)], 7.11—7.25 (m, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 26.0, 26.1, 27.1, 27.3, 55.1, 55.4, 56.9, 57.1, 120.8, 120.9, 121.1, 121.2, 121.5, 126.3, 126.4, 126.5, 126.8, 144.8, 144.9, 146.1, 146.2; IR (KBr) 3072, 3020, 2980, 2948, 2868, 1584, 1470, 1118, 1026, 1014, 1004, 958, 756, 508 cm^{-1}.

Preparation of Isomeric Episulfides (6a—c): A solution of a mixture of isomeric thiadiazolines **5a—c** (1.00 g, 2.91 mmol) in toluene (20 ml) was heated under reflux for 18 h. The mixture was evaporated under reduced pressure. The residue was placed on a column of silica gel and the column was eluted with $CHCl_3$/hexane (1 : 3) to give 277 mg (30%) of **6a**, 449 mg (49%) of **6c**, and 136 mg (15%) of **6b** in this order.

6a: Colorless needles; mp 242—243 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.20—1.28 (m, 4H), 2.20—2.27 (m, 4H), 2.97 (s, 4H), 6.64—6.76 (m, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 27.1, 49.7, 72.3, 120.1, 125.6, 144.6; IR (KBr) 3040, 2968, 2932, 2904, 2868, 1470, 1138, 1012, 764, 730, 468 cm^{-1}; MS *m/z* 316 (M^+; 79%), 288 (100%). Found: C, 83.26; H, 6.35%. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37%.

6b: Colorless needles; mp 247—248 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.47—1.51 (m, 4H), 2.26—2.34 (m, 4H), 3.30 (s, 4H), 7.10—7.13 (m, 4H), 7.18—7.21 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 27.5, 50.4, 78.8, 120.8, 125.9, 147.1; IR (KBr) 3070, 3060, 2964, 2868, 1478, 1464, 1448, 1276, 1166,

1096, 780, 740, 510 cm^{-1}; MS *m/z* 316 (M^+; 100%). Found: C, 83.35; H, 6.38%. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37%.

6c: Colorless needles; mp 229—230 °C (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ = 0.93—1.01 (m, 2H), 1.08—1.17 (m, 2H), 1.35—1.40 (m, 2H), 2.23—2.31 (m, 2H), 3.12 (m, 4H), 7.06—7.10 (m, 2H), 7.14—7.18 (m, 4H), 7.21—7.24 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 26.3, 27.2, 48.8, 50.6, 74.7, 75.2, 120.6, 120.8, 125.8, 126.3, 145.8, 146.6; IR (KBr) 3024, 2980, 2944, 2868, 1468, 1452, 1282, 1168, 1120, 774, 738, 728, 504 cm^{-1}; MS *m/z* 316 (M^+; 92%), 288 (100%). Found: C, 83.21; H, 6.41%. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37%.

***syn*-Bibenzonorbornenylidene (1a) from the Episulfide 6a:** A mixture of **6a** (270 mg, 0.85 mmol) and PPh_3 (1.70 g, 6.48 mmol) was heated at 120 °C for 20 h. The resulting mixture was dissolved in $CHCl_3$, washed with a 15% H_2O_2 solution and water, dried over $MgSO_4$, and evaporated. The residue was placed on a column of silica gel and the column was eluted with $CHCl_3$/hexane (1 : 3) to give 217 mg (89%) of **1a**: colorless needles; mp 212—213 °C (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ = 1.22—1.26 (m, 4H), 1.84—1.93 (m, 4H), 3.66 (s, 4H), 6.96—6.99 (m, 4H), 7.06—7.09 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 27.4, 44.5, 119.9, 125.4, 134.3, 146.9; IR (KBr) 3044, 2976, 2940, 2868, 1468, 1460, 1108, 752, 712, 652, 546, 474 cm^{-1}; MS *m/z* 284 (M^+; 33%), 256, (81%), 128 (100%). Found: C, 93.11; H, 7.14%. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09%.

***syn*-Bibenzonorbornenylidene (1a) from the Episulfide 6b:** A mixture of **6b** (100 mg, 0.32 mmol) and PPh_3 (495 mg, 1.89 mmol) was heated at 120 °C for 12 h. The resulting mixture was purified as described above to give 79 mg (88%) of **1a**.

***anti*-Bibenzonorbornenylidene (1b) from the Episulfide 6c:** A mixture of **6c** (373 mg, 1.18 mmol) and PPh_3 (1.77 g, 6.75 mmol) was heated at 120 °C for 20 h. The resulting mixture was purified as described above to give 303 mg (90%) of **1b**: colorless needles; mp 270—271 °C (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ = 1.10—1.17 (m, 4H), 1.72—1.84 (m, 4H), 3.65 (s, 4H), 7.05—7.08 (m, 4H), 7.14—7.17 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 27.0, 44.4, 119.8, 125.4, 134.1, 147.5; IR (KBr) 3060, 2968, 2940, 2864, 1462, 1444, 1276, 1108, 820, 752, 652, 546, 456 cm^{-1}; MS *m/z* 284 (M^+; 61%), 256 (100%), 128 (66%). Found: C, 92.82; H, 7.08%. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09%.

X-Ray Crystallographic Analysis of Episulfides 6a and 6c and Alkenes 1a and 1b: Crystal data are given in Table 1. The data were recorded on a Mac Science DIP3000 diffractometer equipped with a graphite monochrometer. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo $K\alpha$ radiation (λ = 0.71073 Å) and the data reduction was made by the MAC DENZO program system. Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares.

The complete F_o—F_c data together with relevant data including bond distances and angles have been deposited as Document No. 73056 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been also deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers 147037—147040.

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Table 1. Crystal Data of **6a**, **6c**, **1a**, and **1b**

	6a	**6c**	**1a**	**1b**
Chemical formula	$C_{22}H_{20}S$	$C_{22}H_{20}S$	$C_{22}H_{20}$	$C_{22}H_{20}$
Formula weight	316.47	316.47	284.40	284.40
Crystal form	Needles	Needles	Needles	Needles
Crystal size/mm^3	$0.27 \times 0.13 \times 0.12$	$0.24 \times 0.14 \times 0.12$	$0.26 \times 0.12 \times 0.10$	$0.42 \times 0.10 \times 0.08$
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	16.927(2)	6.419(1)	6.448(1)	6.371(1)
b/Å	8.989(1)	10.998(2)	23.451(3)	22.465(2)
c/Å	13.799(2)	12.820(2)	10.508(1)	10.812(2)
α/deg		111.657(6)		
β/deg	127.823(4)	92.903(9)	94.072(7)	90.747(7)
γ/deg		101.966(8)		
V/$Å^3$	1658.5(3)	814.8(2)	1584.9(3)	1547.3(3)
Z	4	2	4	4
D_{calc}/Mg m^{-3}	1.267	1.290	1.192	1.221
No. of measured reflections	2400	3998	3992	4354
No. of independent reflections	2306	3678	3465	3804
No. of observed reflections	1992	2662	2171	2516
No. of parameters	278	258	279	279
R	0.046	0.052	0.055	0.059
R_w	0.057	0.060	0.051	0.053
GOF	1.534	1.100	1.897	1.852
$\Delta\rho_{max}$/e $Å^{-3}$	0.55	0.67	0.58	0.72
$\Delta\rho_{min}$/e $Å^{-3}$	−0.45	−0.35	−0.38	−0.42

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