Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. XIX. Sulfur Inversion in 9-[2-(Ethylthiomethyl)phenyl]-9-borabicyclo[3.3.1]nonane Proceeds via Dissociative Mechanism[1)]

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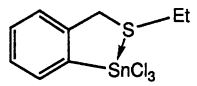
Kinetic parameters for sulfur inversion in the title compound were determined by the dynamic NMR method in CD_2Cl_2 as follows: $\Delta H^{\neq}$ 14.2±0.1 kcal mol^{-1}, $\Delta S^{\neq}$ 11.3±0.3 cal mol^{-1} K^{-1}, $\Delta G^{\neq}_{233}$ 11.6 kcal mol^{-1}. The large and positive entropy of activation suggests that the inversion takes place through dissociative mechanisms. Comparison of the rate constants obtained with multiple probes shows that the rotation about the C_{Ph}–B bond requires further energy after the dissociation of the S–B bond. The solvent effect on the sulfur inversion is small but distinct; the more polar a solvent, the higher the barrier to the inversion. Dynamic behaviors of a related compound are also discussed.

Although inversion at a trivalent sulfur atom is one of the interesting phenomena in stereochemistry, there have been few general methods to investigate mechanisms of the inversion. Dynamic NMR spectroscopy was found to be a useful technique in studying sulfur inversion, especially in coordination compounds.[2,3)] Recently, we reported sulfur inversion in sulfonium salts,[4)] thioether–Lewis acid complexes,[5)] and platinum(II) complexes[6)] by the use of this method. These results are generalized that entropy of activation ($\Delta S^{\neq}$) is a convenient guide for diagnosing the mechanisms of sulfur inversion: Entropy of activation is large positive if the bond dissociation is the rate-limiting step (dissociative mechanism), whereas it is nearly zero if sulfur inversion takes place without bond scission (pyramidal inversion).

An organostannane compound **1** was one of the examples in the former case, but analogous boron compound **2** failed to show dynamic processes even at −90 °C due to low barrier to the S–B bond dissociation.[5)] Many of organoboron–thioether adducts were known to be unstable because of the weak basicity of the sulfur atom toward the boron atom.[7)] We expected that introduction of a boron atom bearing two alkyl groups should enhance S–B bond energy with respect to the boronate S–B bond. Our recent work revealed that the boron atom in 9-borabicyclo[3.3.1]-9-nonyl (9-BBN) group, which has unusual stability as a diakylboryl group,[8)] was a stronger Lewis acid toward amine ligands than that in boronates.[1,9)] We decided to use this boron atom as an acceptor and chose 9-[2-(ethylthiomethyl)phenyl]-9-BBN (**3**) for our study on the dissociation of the S–B bond.



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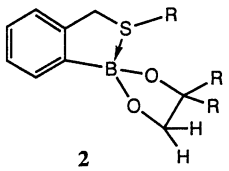

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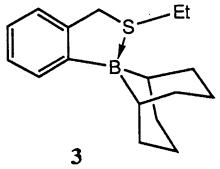


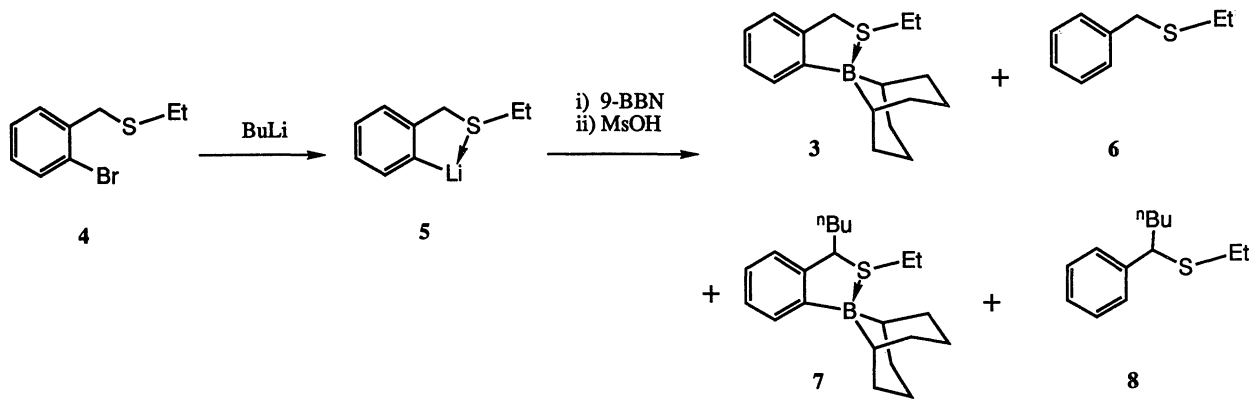
3

We have been interested in solvent effects on the rates of sulfur inversion as well. The barriers for the inversion in platinum(II)–thioether complexes are independent of solvents, in which the sulfur inverts without bond dissociation.[6)] On the other hand, there is no available information about solvent effects in dissociative mechanisms. Polar solvents decelerate the dissociation of coordination bonds involving a boron atom from our experiences[1,9)] and the same effects are expected in the dissociation of the S–B bond. In order to make the relationship between the inversion mechanism and solvent effects clear, we observed inversion processes of compound **3** in various solvents.

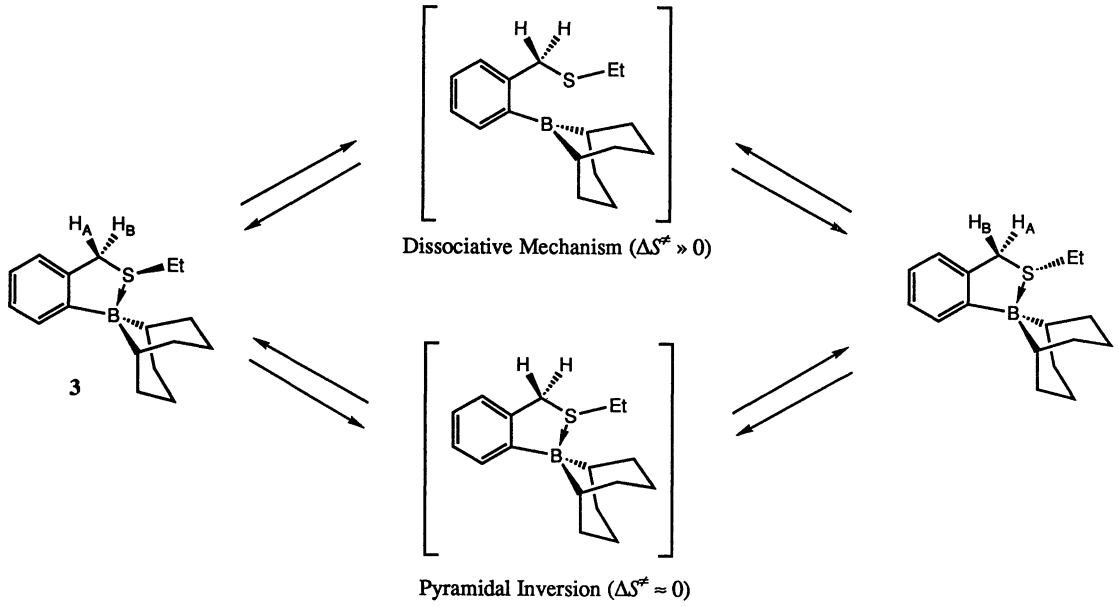
Results and Discussion

Synthesis and NMR Spectra of 3. Compound **3** was prepared in a modified procedure of the known method for the syntheses of 9-aryl-9-BBN's[10)] shown in Scheme 1. A solution of ethyl *o*-lithiobenzyl sulfide (**5**), prepared from 1-bromo-2-(ethylthiomethyl)benzene (**4**) and butyllithium, was treated with 9-BBN followed by methanesulfonic acid to give an oily mixture containing the desired compound. The reaction products were separated by HPLC and subsequent recrystallization afforded **3** in 19% yield as white crystals, which were air stable and soluble in ordinary organic solvents.

Other three products were identified as **6** (39%), **7** (7%), and **8** (4%) from their NMR and mass spectra: Compound **6** is a hydrolysis product of **5** and compounds **7** and **8** are butylated products of **3** and **6**, respectively. We believe that compounds **7** and **8** are formed in the following way. The benzylic protons in **3** and **6** are firstly lithiated by lithium hydride that results



Scheme 1.



Scheme 2. Possible mechanisms for the sulfur inversion in compound **3**.

from treatment of **5** with 9-BBN, although it is difficult to rule out that other lithium species react with them because various lithium sources may exist in the reaction mixture. Then butyl bromide derived from butyllithium attacks the benzylic positions to form compounds **7** and **8**. Prolonged stirring before the addition of methanesulfonic acid increased yields of the butylated compounds; this fact supports the mechanisms mentioned above.

Compound **3** possesses some diastereotopic pairs of protons and carbons which exchange their sites on the topomerization shown in Scheme 2. The benzylic methylene protons exhibited a sharp singlet at room temperature. With lowering the temperature, the signal began to broaden and became an AB quartet signal at −70 °C in CD_2Cl_2. Other proton signals except for the aromatic and the methyl ones also exhibited line shape changes in the temperature range. Carbon signals due to the 9-BBN group were broad even at room temperature and separated into eight signals at −70 °C. These observations suggests that the sulfur atom coordinates to the boron atom in **3** at low temperatures. The sulfur inversion takes place faster than the NMR time scale at room temperature and this process is frozen at −70 °C.

The chemical shift of ^{11}B NMR (**3**: 14.4 ppm) supports a coordinated structure as well. This value is typical for a tetrahedral boron and at a higher field than those in trialkylboranes.[11] The high field shifts caused by sulfur coordinations were observed in 9-halo-9-BBN complexes with dimethyl sulfide relative to free 9-halo-9-BBN's.[12]

Kinetic Parameters and Mechanism of Sulfur Inversion. We firstly selected benzylic methylene protons as a probe for the observation of dynamic processes at the

sulfur atom. Altough the methylene protons in the ethyl group also seemed to satisfy the requirement as a probe, we excluded them because of overlapping of the signals with those of the ring protons. The total line shape analyses were carried out with the use of DNMR3K program[13] and observed and simulated NMR signals for the benzylic methylene protons are shown in Fig. 1. Eyring plot of rate constants thus obtained affords kinetic parameters for the topomerization (Table 1).

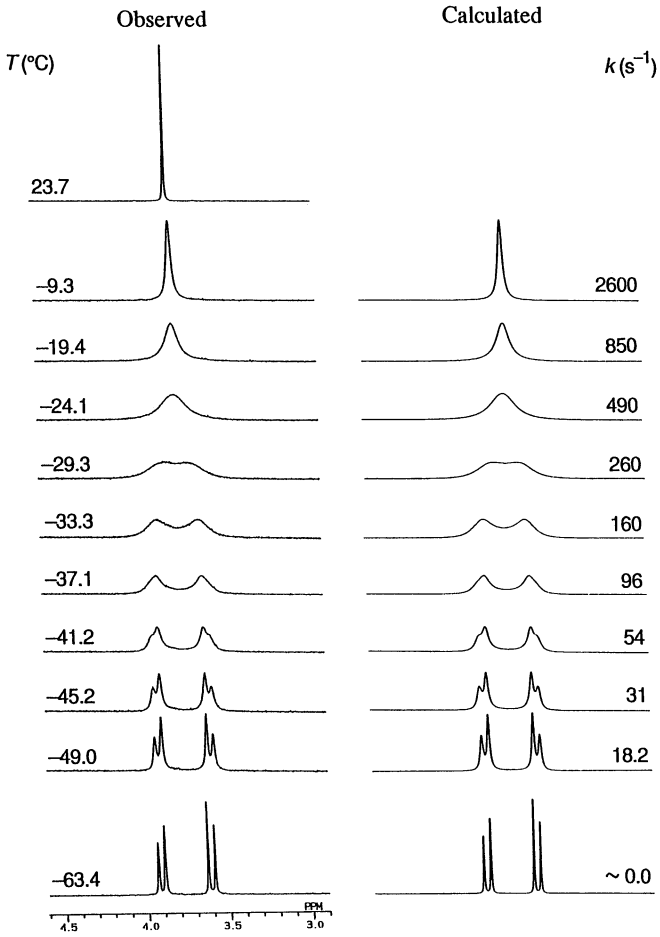


Fig. 1. Observed (solvent CD_2Cl_2) and calculated (DNMR3K program) line shapes for the benzylic methylene protons in compound **3**.

Entropy of activation is large positive as is expected for the dissociative mechanism, in which the ground state is ionic and the transition state is less ionic. Consequently, the dissociation of the S–B bond is the rate-limiting step for the topomerization of the benzylic methylene protons and the topomerization completes after the recombination from another side to form an S–B bond (Scheme 2). Strictly speaking, the rate constants of the topomerization should be doubled when we take account of the dissociation of the S–B bond. The dissociated sulfur atom recoordinates to the boron atom at the same site or at the other site with the same probabilities.

The S–B bond in **3** is more than 3 kcal mol^{-1} stronger than those in boronates (**2**)[15] and ca. 4 kcal mol^{-1} weaker than that in 3,3,4,4-tetramethylthiolane-boron tribromide complex.[5] These results are consistent with the general order of Lewis acidity of the boron atom: trihaloborane>trialkylborane>boronate.[7]

We have reported that, in platinum(II)-thioether complexes, the sulfur inversion takes place without scission of the Pt–S bond.[6] The results reported here contrast in the mechanisms of inversion. In the case of platinum, the pπ–dπ interaction is possible to stabilize the planar transition state for inversion. In the case of boron, the d-orbitals are of so high energy that such an interaction to stabilize the planar transition state for inversion is not effective. These differences must be responsible to the difference in the mechanisms of the sulfur inversion.

Comparison of Kinetic Parameters Obtained from Multiple Probes. We could also obtain kinetic parameters for the topomerization from diastereotopic proton and carbon pairs in the 9-BBN moiety in dichloromethane-d_2, these data being compiled in Table 1. Three probes that follow were used other than the benzylic methylene proton probe: The protons and carbons at 1,5-positions (1,5-H and 1,5-C) and the carbons at 3,7-positions (3,7-C) in the 9-BBN group.

The rate constants obtained from 3,7-C are ca. 7 times smaller than that obtained from the benzylic methylene proton probe. Namely, the topomerization observed by 3,7-C probe requires additional energy, 0.9 kcal mol^{-1}, compared with the latter probe. The site

Table 1. Kinetic Parameters for the Topomerization Obtained with Multiple Probes in Compound **3**[a]

Probe	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{233}$	k_{233}	r[b]
	kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	s^{-1}	
^{1}H CH_2[c]	14.2±0.1	11.3±0.4	11.6	65	0.9999
^{1}H CH_2[c,d]	14.3±0.3	11.9±1.3	11.6	64	0.9998
^{1}H 1,5-*H*			11.5 (245 K)[e]		
^{13}C 3,7-*C*	15.3±0.8	11.9±3.2	12.5	8.7	0.9993
^{13}C 1,5-*C*			11.5 (249 K)[e]		

a) 1 cal=4.184 J. Concentration ca. 40 and ca. 400 mmol dm^{-3} for ^{1}H and ^{13}C probes, respectively, unless otherwise mentioned. b) Correlation coefficient. c) Benzylic methylene protons. d) Concentration 400 mmol dm^{-3}. e) $\Delta G^{\neq}$ at coalescence temperature (T_c) obtained by the coalescence method.

Table 2. Solvent Effects on the Kinetic Parameters for the Topomerization of Benzylic Methylene Protons in Compound **3**

Solvent	ε[a)]	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{233}$	k_{233}	r
		kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	s^{-1}	
$C_6D_{11}CD_3$[b)]	2.02	13.5±0.3	9.4±1.2	11.3	129	0.9997
Toluene-d_8	2.38	14.3±0.3	11.4±0.9	11.7	54	0.9998
$(C_2D_5)_2O$	4.20	15.1±0.4	15.1±1.0	11.6	61	0.9998
THF-d_8	7.58	14.7±0.2	11.9±0.7	11.9	31	0.9999
CD_2Cl_2	8.93	14.2±0.1	11.3±0.4	11.6	65	0.9999
Acetone-d_6	20.56	14.5±0.3	11.4±0.9	11.8	42	0.9998
DMF-d_7	36.71	14.6±0.2	10.6±0.8	12.2	20	0.9999

a) Dielectric constants for non-deuterated solvents from Ref. 20. b) Methylcyclohexane-d_{14}.

exchange of 3,7-C requires bond rotaion about the C_{Ph}–B as well as the dissociation of the S–B bond. Although the sulfur inversion without the S–B bond breakage might explain the discrepancy of the rates, this process is eliminated from being the course for the observed topomerization because the inversion took place in dissociative mechanisms as judged from the value of entropy of activation mentioned above. On a steric point of view, pyramidal inversion seems to be an unfavorable process; steric hindrance between the 9-BBN group and the ethyl group must be serious at the transition state for the pyramidal inversion.

The differences in the rates are due to hindered rotation about the C_{Ph}–B bond after the dissociation of the S–B bond. Thus the rate-limiting step for the exchange of 3,7-C is the C–B bond rotation rather than the S–B bond dissociation. A 9-BBN group, in which wing protons overhang outside, is known to be bulky and its bulkiness is superior to that of a *t*-butyl group. It is probable that the rotation about the C_{Ph}–B bond is slow though there is no report on restricted rotation in an *o*-substituted 9-aryl-9-BBN.

The kinetic parameters for the exchanges of 1,5-H and 1,5-C were only determined by the coalescence method because their signals were very broad owing to spin-spin couplings with ^{10}B and ^{11}B. Both of the free energies of activation at the coalescence temperature are almost the same as that obtained from the benzylic methylene probe. This result is natural if one considers the topomerization mechanism; the site exchange of 1,5-positions completes by the sulfur inversion regardless of the C–B bond rotation.

Solvent Effects on the Dissociation of S–B Bond. The rates of dissociation in various solvents are listed in Table 2. As expected, an increase in solvent polarity tends to decelerate the dissociation of the S–B bond. The same effect in N–B bond dissociation has been explained on the basis of better stabilization of the polar ground state in polar solvents than the less polar transition state.[1,9)] It is reasonable to assume that this explanation is also the case for the S–B bond dissociation.

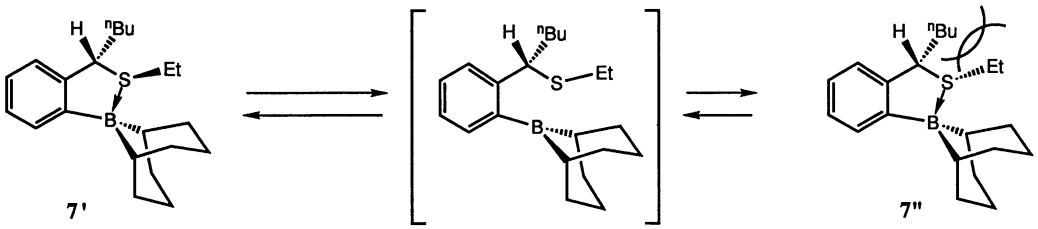
A careful comparison of the rate constants shows that the solvent effect on the S–B bond dissociation in **3** is smaller than that on the N–B bonds: a relative rate constant in methylcyclohexane-d_{14} and DMF-d_7, k(methylcyclohexane-d_{14})/k(DMF-d_7), is 6.5 in **3**, whereas it is 22 in 9-[2-(diethylaminomethyl)phenyl]-9-BBN (**9**).[1)] The small solvent effect can be interpreted in terms of polarity of a coordination bond. Since an S–B bond is less ionic than an N–B bond, the solvation which stabilizes the ground state in the dissociation process is less important in the S–B bond case than that in the N–B. Anyway, there are unambiguous solvent effects on the dissociation of the S–B bond.

In contrast, there are little solvent effects on the sulfur inversion in platinum(II)–thioether complexes, in which the inversion took place without bond dissociation.[6)] Therefore, solvent effects can be a clue to distinguish the two mechanisms of sulfur inversion; presence of solvent effects described above in the dissociative mechanism and absence of solvent effect in the pyramidal inversion. It is necessary to evaluate the solvent effects carefully because the difference in rate constants tend to be small in the dissociative mechanism.

Solvent assisted dissociation (S_N2 type dissociation) is observed for the N–B bond dissociation in an amine–boronate complex.[9)] This assistance seems to be improbable in the 9-BBN system, compound **3** as well as **9**, due to steric hindrance of the bicyclic frame work. The rate constants of the dissociation obtained in donor solvents, diethyl-d_{10} ether, THF-d_8, and DMF-d_7, are not apart from those expected from their polarities. This finding supports the non-assisted dissociation mechanism.

Dynamic Behaviors in 7. The structural feature and some dynamic behaviors of the by-product **7** are also interesting. The structure was determined from its NMR and mass spectra (M^+ 328), these data suggesting existence of an extra butyl group compared with the structure of **3**. Since this compound has a chiral center at the benzylic carbon, two diastereomers should exist if the dissociation of S–B bond is negligibly slow.

The NMR spectra observed at various temperature exhibited line shape changes. This compound gave broad proton and carbon signals in the aliphatic region



Scheme 3. Topomerization process between diastereomers in compound **7**.

at room temperature and these signals became sharp at −40 °C. These dynamic processes are also caused by the S–B bond dissociation shown in Scheme 3.

The NMR spectrum observed at −40 °C where the dynamic process is virtually frozen suggests that this compound exist in two forms, the major isomer being in 97% and the minor in 3% from integrated intensities of signals due to the benzylic methine proton. We assume that **7'** should be the major isomer because another isomer **7"**, in which the butyl group and the ethyl are eclipsing, is sterically unfavorable. The population of the isomers shows that the major form is more stable by 1.6 kcal mol^{-1} than the minor one. The carbon signals observed at −40 °C are in accord with the structure of **7'**.

The signals due to the benzylic methine proton showed line broadening at 0 °C and this change is interpreted in terms of the interconversion between the two isomers. Roughly estimated free energy of activation for the isomerization is 12 kcal mol^{-1} from the major isomer to the minor. This barrier is comparable to that for the S–B bond dissociation in **3**. This is in accord with the idea that the S–B bond scission is the rate-limiting step for the diastereomerization.

Experimental

Melting points are uncorrected. Silica gel 60 (Merck, 70—230 mesh) and Silica gel 60 F_{254} (Merck, 0.25 mm) were used for column and thin-layer chromatography, respectively. Preparative HPLC was carried out with a Hitachi L-6250 intelligent pump using a Chemcosolb Si column (5 μ, 25 mmϕ×500 mm). Elemental analyses were performed by a Perkin-Elmer 240C analyser. Mass spectra were measured with a JEOL JMS-DX303 spectrometer.

NMR Measurement and Line Shape Analysis. ^{1}H and ^{13}C NMR spectra were measured on a JEOL GSX-400 spectrometer operating at 399.8 MHz and 100.5 MHz, respectively. Temperatures were calibrated with a methanol sample. The concentration of the solution was ca. 40 mmol dm^{-3} and ca. 400 mmol dm^{-3} for ^{1}H and ^{13}C NMR measurement, respectively. The line shape analysis was performed by DNMR3K program.[13] Coupling constants and chemical shift differences were measured at several points where rates were almost zero. The chemical shift differences were linearly correlated with temperature, but the coupling constants were constant at every temperature. Spin-spin relaxation times (T_2) were estimated from the line width of exchanging signals at the slow exchange limit and line shapes of non-exchanging signals at the temperature where the exchange takes place. Input parameters for the simulation for the benzylic methylene protons (AB⇄BA) are listed in Table 3. The analyses for the carbon probe (3,7-C) were performed similarly under the A⇄X exchanging system with the use of the following parameters: $\Delta\nu$=54.5 Hz, T_2=0.17 s. The rate constants obtained are shown in Table 4. The barrier for the topomerization of 1,5-H and 1,5-C were determined by the coalescence method. The coalescence temperatures (T_c) and chemical shift differences ($\Delta\nu$) are −28±1 °C and 129.6 Hz for the 1,5-H and −24±1 °C and 201.0 Hz for the 1,5-C probe, respectively.

Table 3. Temperature Dependence of the Chemical Shift Difference, Coupling Constant, and T_2 of Benzylic Methylene Protons in Compound **3**

Solvent	$\Delta\nu_{AB}$/Hz[a]	J_{AB}/Hz[b]	T_2/s[c]
$C_6D_{11}CD_3$	0.609t+187.2	−15.9	0.14—0.16
Toluene-d_8	205.9[e]	−16.3	0.14—0.15
$(C_2D_5)_2O$	0.626t+156.3	−16.3	0.11—0.13
THF-d_8	0.594t+100.1	−16.2	0.13—0.16
CD_2Cl_2	0.323t+140.3	−16.4	0.18—0.19
CD_2Cl_2[d]	0.365t+142.6	−16.4	0.14—0.16
Acetone-d_6	0.486t+76.5	−16.4	0.17—0.18
DMF-d_7	0.246t+59.3	−16.5	0.13—0.16

a) Chemical shift differences between benzylic methylene protons (AB signal): $\Delta\nu_{AB}$/Hz=xt/°C+y. b) Coupling constants between A and B protons. These were constant throughout the temperature range. c) Spin-spin relaxation times for the signals. d) Concentration ca. 400 mmol dm^{-3}. e) Constant throughout the temperature range.

^{11}B NMR spectra were measured on the JEOL GSX-400 spectrometer with a multinuclear tunable probe operating at 128.2 MHz. The chemical shifts are given to an external BF_3:OEt_2 (δ=0) reference.

9-[2-(Ethylthiomethyl)phenyl]-9-borabicyclo[3.3.1]nonane (3). To a solution of 3.34 g (14.4 mmol) of 1-bromo-2-(ethylthiomethyl)benzene[17] in ether (20 ml) was added 9.25 ml (14.4 mmol) of a 1.5 mol dm^{-3} hexane solution of butyllithium at −30 °C under a nitrogen atmosphere. The mixture was allowed to warm up to 0 °C and added to 28.8 ml (14.4 mmol) of a 0.5 mol dm^{-3} THF solution of 9-borabicyclo[3.3.1]nonane (Aldrich Co. Inc.) at 0 °C during the course of 1 min. Immediately after the addition, methanesulfonic acid (1.39 g, 14.4 mmol) was added at 0 °C and the mixture was stirred for 1 h at room temperature. The precipitate was filtered off by a glass filter and the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane to give 2.34 g of a nonpolar mixture (colorless oil),

Table 4. Rate Constants of Topomerization Obtained with the Proton Probe (Benzylic Methylene Protons) in Compound **3**

Solvent	k/s^{-1} (temperature/°C)
$C_6D_{11}CD_3$	20.5 (−53.7), 39 (−49.1), 70 (−44.2), 135 (−39.6), 215 (−35.7), 350 (−31.8), 610 (−27.4), 1000 (−23.0), 1800 (−18.0)
Toluene-d_8	16.8 (−48.2), 34.0 (−43.3), 67 (−38.3), 135 (−33.4), 240 (−28.3), 440 (−23.4), 830 (−18.5), 1450 (−13.5), 2400 (−8.4)
$(C_2D_5)_2O$	13.2 (−50.3), 22.5 (−46.3), 44 (−42.3), 87 (−37.8), 162 (−33.3), 300 (−28.3), 580 (−23.4), 1050 (−18.5), 1850 (−13.4), 3500 (−8.5)
THF-d_8	9.8 (−48.0), 19.0 (−43.4), 41.0 (−38.2), 78 (−33.4), 145 (−28.4), 270 (−23.4), 560 (−17.4), 1600 (−8.4)
CD_2Cl_2	18.2 (−49.0), 31.0 (−45.2), 54 (−41.2), 96 (−37.1), 160 (−33.3), 260 (−29.3), 490 (−24.1), 850 (−19.4), 2600 (−9.3)
CD_2Cl_2[a]	10.6 (−52.2), 28.0 (−45.9), 58.5 (−40.8), 118 (−35.7), 225 (−30.6), 425 (−25.4), 750 (−20.3)
CD_2Cl_2[b]	8.0 (−40.8), 18 (−35.7), 37 (−30.6), 70 (−25.4), 125 (−20.3), 400 (−10.2)
Acetone-d_6	6.8 (−52.7), 12.8 (−48.2), 22.1 (−44.3), 39.0 (−40.3), 68 (−36.3), 122 (−32.0), 220 (−27.5), 440 (−21.4), 920 (−15.5)
DMF-d_7	11.8 (−43.4), 23.5 (−38.9), 42.5 (−34.5), 78 (−29.8), 135 (−25.4), 230 (−21.0), 390 (−16.5), 650 (−11.9)

a) Concentration ca. 400 mmol dm^{-3}. b) Obtained with the carbon probe (3,7-C).

which consisted of four major products (R_f=0.42, 0.38, 0.36, and 0.31. eluent: hexane) and other minor products. The fractions containing the desired compound (R_f=0.36) were purified by HPLC (hexane as an eluent). Recrystallization from hexane-ether afforded 0.74 g (19%) of the desired compound as white crystals. Mp 116.0—118.0 °C. Found: C, 75.13; H, 9.41%; M^+, 272. Calcd for $C_{17}H_{25}BS$: C, 75.00; H, 9.26%; M^+, 272. ^{1}H NMR ($CDCl_3$) δ=1.00 (2H, br s), 1.28 (3H, t, J=7.4 Hz), 1.63—1.72 (2H, br m), 1.76—2.10 (10H, br m), 2.34 (2H, q, J=7.5 Hz), 3.89 (2H, s), 7.08—7.14 (2H, m), 7.19 (1H, dt, J=2.1 and 6.8 Hz), 7.69 (1H, d, J=7.5 Hz). ^{13}C NMR ($CDCl_3$)[18] δ=12.1, 23 (very broad, coupled with ^{10}B and ^{11}B), 24.1, 24.5, 32.8 (br), 37.2, 125.0, 125.1, 126.3, 132.3, 138.5. ^{11}B NMR ($CDCl_3$) δ=14.4.

Following three products were also identified.

9-[2-(1-Ethylthiopentyl)phenyl]-9-borabicyclo[3.3.1]nonane (7). **7** (R_f=0.42) was isolated by recrystallization from hexane. Yield 0.38 g (7%), mp 78.5—80.0 °C. Found: C, 76.80; H, 10.24%; M^+, 328. Calcd for $C_{21}H_{33}BS$: C, 76.81; H, 10.13%; M^+, 328. ^{1}H NMR ($CDCl_3$, r.t.) δ=0.94 (3H, t, J=7.4 Hz), 0.96 (2H, br), 1.32 (3H, t, J=7.5 Hz), 1.34—2.48 (19H, m), 2.53 (1H, m), 3.95 (1H, m), 7.08 (1H, d, J=7.2 Hz), 7.12 (1H, dt, J=1.0 and 7.2 Hz), 7.19 (1H, dt, J=1.4 and 7.2 Hz), 7.69 (1H, d, J=7.2 Hz). (CD_2Cl_2, −40 °C) δ=0.72 (1H, br s), 0.84 (3H, t, J=7.4 Hz), 0.93 (1H, br s), 1.24 (3H, t, J=7.4 Hz), 1.16—2.10 (18H, m), 2.33 (1H, m), 2.48 (1H, m), 3.89 (1H, dd, J=1.4 and 7.4 Hz, benzylic methine proton for the major isomer), 4.36 (br m, benzylic methine proton for the minor isomer), 6.98—7.17 (3H, m), 7.58 (1H, d, J=7.2 Hz). ^{13}C NMR ($CDCl_3$, r. t.)[18] δ=12.7, 13.9, 22.3, 24.5 (br), 25.5, 30.9, 21—38 (very broad), 56.5, 124.9, 125.0, 126.2, 132.5, 144.1. (CD_2Cl_2, −40 °C) δ=12.4, 13.9, 21.7 (br), 22.3, 24.0, 24.7, 25.4, 27.2 (br), 30.0, 30.9, 31.1, 32.9, 35.0, 37.4, 56.2, 125.0, 124.3, 126.0, 132.4, 144.3, 154.1. ^{11}B NMR ($CDCl_3$) δ=12.9. The free energy of activation for the topomerization between the two diastereomers was determined by the coalescence method with the signals due to benzylic methine protons (δ=3.89 and 4.36) in dichloromethane-d_2. The coalescence temperature was −17± 3 °C and the chemical shift difference was 184.8 Hz. The population of the minor isomer was 3.1% at −40 °C determined from the integration of the signals and the difference in free energies was 1.6 kcal mol^{-1} at the temperature. Other signals due to the minor isomer were not assigned because of various ambiguity.

Ethyl 1-Phenylpentyl Sulfide (8). **8** (R_f=0.38) was not isolated and its yield (0.13 g or 4%) was determined from the signal intensity of ^{1}H NMR. This compound was synthesized by another method as follows. A solution of α-lithiobenzyl ethyl sulfide (13.1 mmol) in ether (20 ml) prepared from benzyl ethyl sulfide and butyllithium in an ordinary manner was treated with 1-bromobutane (15.7 mmol) at 0 °C. Addition of 1 mol dm^{-3} HCl (20 ml) gave the desired sulfide (2.39 g, 87%) together with recovered benzyl ethyl sulfide (0.17 g, 9%). Bp 92—94 °C/0.4 mmHg (1 mmHg=133.322 Pa). Found: M^+, 208.1274. Calcd for $C_{13}H_{20}S$: M^+, 208.1285. ^{1}H NMR ($CDCl_3$) δ=0.84 (3H, t, J=7.0 Hz), 1.14 (3H, t, J=7.5 Hz), 1.17—1.37 (4H, m), 1.77—1.92 (2H, m), 2.25 and 2.29 (2H, AB part of the ABX_3 system, J_{AX}=J_{BX}=7,5 Hz, J_{AB}=12.3 Hz), 3.77 (1H, dd, J=6.5 and 8.6 Hz), 7.19—7.34 (5H, m). ^{13}C NMR ($CDCl_3$) δ=13.8, 14.4, 22.4, 24.8, 29.8, 36.2, 49.4, 126.8, 127.7, 128.3, 143.1.

Benzyl Ethyl Sulfide (6). **6** (R_f=0.31), which was obtained in 39% yield, was identified by comparison of ^{1}H NMR data with an authentic sample prepared by a standard method.[19] ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, t, J=7.4 Hz), 2.44 (2H, q, J=7.4 Hz), 3.72 (2H, s), 7.21—7.33 (5H, m). ^{13}C NMR ($CDCl_3$) δ=14.3, 25.1, 35.8, 126.8, 128.4, 128.8, 138.5.

When the reaction mixture was stirred for 1 h at room temperature before the addition of methanesulfonic acid in the procedure of synthesis of **3**, yields of the products were 20, 30, 11, and 23% for **3**, **6**, **7**, and **8**, respectively. Separation of the products was tedious.

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