diphenylmethane the reference acids were fluorene (pK = 24.4 ± 0.2)[3] and 4-benzylpyridine (pK = 25.3 ± 0.2).[8] The pK values for these and other acids are recorded in Table IV.

Acknowledgment. We are grateful to Prof. R. Reed for generously providing the electrosynthetic cell and valuable information.

Registry No. (Diphenylmethyl)lithium, 881-42-5; [(pyridin-3-yl)phenylmethyl]lithium, 97254-18-7; [(pyridin-2-yl)phenylmethyl]lithium, 56501-99-6; [(pyridin-4-yl)phenylmethyl]lithium, 81771-00-8; (triphenylmethyl)lithium, 733-90-4; [(pyridin-3-yl)-diphenylmethyl]lithium, 109283-60-5; [(pyridin-2-yl)diphenylmethyl]lithium, 83425-78-9; [(pyridin-4-yl)diphenylmethyl]lithium, 83425-79-0; anthracene, 120-12-7; 1,1,2,2-tetraphenylethane, 632-50-8; 1,2-di-2-pyridyl-1,2-diphenylethane, 28830-48-0; 1,2-di-3-pyridyl-1,2-diphenylethane, 109283-61-6; 1,2-di-4-pyridyl-1,2-diphenylethane, 24559-23-7; 2-pyridyldiphenylmethane, 3678-70-4; 3-pyridyldiphenylmethane, 3678-71-5; 4-pyridyldiphenylmethane, 3678-72-6.

Supplementary Material Available: CV and DPV for lithio-4-benzylpyridine and anthracene in THF solution and NMR competition spectra (2 pages). Ordering information is given on any current masthead page.

Stereospecific Anti Radical Elimination Reaction from β-Nitro Sulfones

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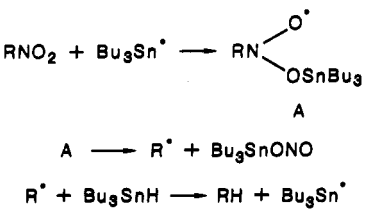
β-Nitro sulfones react with tin radicals to give alkenes, where the nitro and sulfonyl groups are cleaved in an anti stereospecific way. This specificity is lost when the elimination reaction is induced by sodium sulfide. The high stereospecificity of the reaction induced by tin radicals can be interpreted by assuming that the organotin group is close to the nitro group to form a nitroxide radical, which undergoes the stereospecific cleavage of the nitro and sulfonyl groups via successive β-scission of radicals.

Recently, Tanner's group and ours reported a novel reductive cleavage of the carbon–nitrogen bond of aliphatic nitro compounds.[1] It has been proposed that alkyl radicals are formed from anion radical intermediates of nitro compounds, which are formed via a one-electron-transfer process from tin radicals to nitro compounds.[1] Giese also reported that anion radicals are detected by ESR measurements during denitration of nitro sugars with tin radicals,[2] where a tight radical ion pair is proposed as an intermediate.[2] Such anion radicals can be regarded as nitroxide radicals,[3] and the difference between these two species should be very small. Thus, denitration with tributyltin hydride is now believed to proceed via the mechanism shown in Scheme I.

Formation of alkyl radicals from the anion radicals of nitro compounds has been well established in $S_{RN}1$ reactions of nitro compounds.[4] The mechanism of Scheme I is the same as that of $S_{RN}1$ except that a loose radical ion pair is generally involved as an intermediate in $S_{RN}1$. The intermediate A, which is formed by the reaction of tin radicals with nitro compounds, shows a slightly different reactivity from the anion radicals, which are formed by the reaction of nitro compounds with stabilized carbanions or sodium thiophenoxide. For example, the anion radicals formed by the reaction of α-nitro sulfones with stabilized carbanion, sodium thiophenoxide, or 1-benzyl-1,4-dihydronicotinamide (BNAH) undergo the smooth elimination reaction of the sulfinate ion to give α-nitroalkyl radicals.[5,6] On the other hand, tin radicals are inert to

Scheme I



α-nitro sulfones under the usual denitration conditions using tributyltin hydride.[7] Thus, the intermediate A, which is generated by the reaction of tin radicals with nitro compounds, is slightly different from the intermediate of an $S_{RN}1$ reaction of nitro compounds, which is formed in dipolar aprotic solvents with sodium or potassium as a countercation. In order to get more precise information on the reductive cleavage of aliphatic nitro compounds with tin radicals, study of the stereochemistry of the reductive elimination reaction of nitro compounds has been undertaken. Aliphatic nitro compounds such as compounds 1 having radical leaving groups at the β-position undergo reductive cleavage in the radical elimination reaction to give alkenes 2[8] (eq 1). Thus, *vic*-dinitro compounds, β-nitro sulfones, and β-nitro sulfides are converted into alkenes 2 on treatment with Na_2S,[9] Ca/Hg,[10] Bu_3SnH,[11] or NaTeH.[12]

We have found that the elimination reaction of β-nitro sulfones with tin radicals proceeds with high stereospec-

(1) Tanner, D. D.; Blackburn, E. V.; Diaz, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 1557. Ono, N.; Miyake, H.; Tamura, R.; Kaji, A. *Tetrahedron Lett.* **1981**, 1705.

(2) Dupsis, J.; Giese, B.; Hartung, J.; Leising, M.; Korth, H. G.; Sustmann, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 4332.

(3) Reuter, K.; Neumann, W. P. *Tetrahedron Lett.* **1978**, 5235. Davis, A. G.; Hawari, J. A. A. *J. Organomet. Chem.* **1980**, *201*, 221. Sustmann, R.; Korth, H. G. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 95.

(4) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, 734. Kornblum, N. In *The Chemistry of Amino, Nitroso, and Nitro Compounds and Their Derivatives*, Supplement F; Patai, S., Ed.; Wiley: New York, 1982; Part I, pp 361–393.

(5) Kornblum, N.; Boyd, S. D.; Ono, N. *J. Am. Chem. Soc.* **1974**, *96*, 2580.

(6) Ono, N.; Tamura, R.; Tanikaga, R.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1981**, *71*. Wade, P. A.; Hinney, H. R.; Amin, N. V.; Vail, P. D.; Morrow, S. D.; Hardinger, S. A.; Saft, M. S. *J. Org. Chem.* **1981**, *46*, 765.

(7) Ono, N.; Miyake, H.; Kamimura, A.; Hamamoto, I.; Tamura, R.; Kaji, A. *Tetrahedron* **1985**, *41*, 4013.

(8) Ono, N.; Kaji, A. *Synthesis* **1986**, 693.

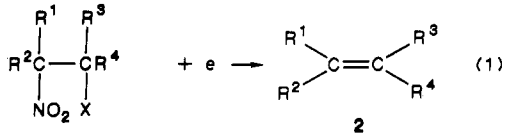
(9) Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4316.

(10) Kornblum, N.; Cheng, L. *J. Org. Chem.* **1977**, *42*, 2944.

(11) Ono, N.; Miyake, H.; Tamura, R.; Hamamoto, I.; Kaji, A. *Chem. Lett.* **1981**, 1139.

(12) Osuka, A.; Simizu, H.; Suzuki, H. *Chem. Lett.* **1983**, 1373.

0022-3263/87/1952-5111$01.50/0

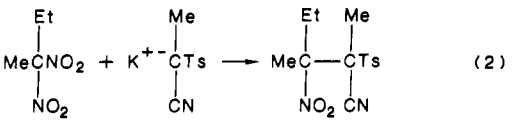


1: X = NO_2, SO_nPh (n = 0, 2)

ificity,[11] but the stereospecificity is lost in the elimination reaction induced by other reducing agents such as Na_2S or NaTeH. In this paper we report full details of this novel radical elimination reaction, which proceeds with high stereospecificity.

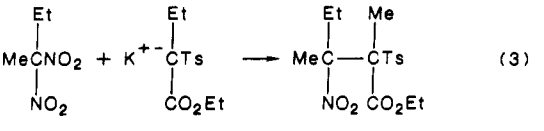
Results and Discussion

Preparation of β-Nitro Sulfides or β-Nitro Sulfones. Tetrasubstituted β-nitro sulfones **3** and **4** were prepared by $S_{RN}1$ reaction of *gem*-dinitro compounds with α-sulfonyl carbanions in dimethyl sulfoxide (DMSO) as shown in eq 2 and 3.[13] Compound **3** or **4** consists of two



(2)

3



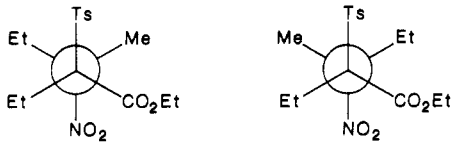
(3)

4

Ts = *p*-toluenesulfonyl

diastereoisomers, and they are readily separated into **3a** and **3b** or **4a** and **4b**, respectively, by column chromatography. The NMR data suggest that compound **3a** or **4a** is the *l* diastereomer, whose asymmetric centers are (*R*,*R*) or (*S*,*S*), and compound **3b** or **4b** is the *u* diastereomer, whose asymmetric centers consists of a pair of *R* and *S*.[14]

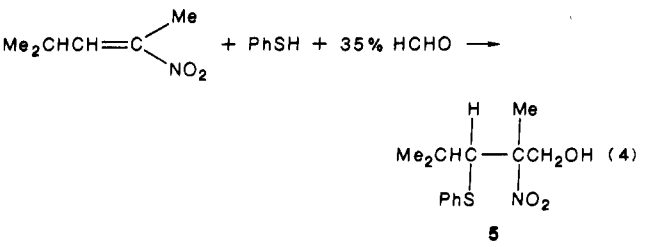
l-**3a** *u*-**3b**



l-**4a** *u*-**4b**

X-ray analysis of compound **3a** was carried out to verify the assignment of the structure by NMR. The structure determined by X-ray analysis is shown in Figure 1 (supplementary material). Bond distances and angles and crystal data of compound **3a** are summarized in Tables I and II, (supplementary material).

Trisubstituted or disubstituted β-nitro sulfones are not prepared by the $S_{RN}1$ reactions, but they are prepared by the oxidation of the corresponding β-nitro sulfides, which are prepared by the addition of thiols to nitroolefins. As separation of diastereoisomers of simple β-nitro sulfides was very difficult, γ-phenylthio β-nitro alcohols **5** were prepared by mixing nitroolefins, thiophenol, and 35% HCHO in the presence of a catalytic amount of tetramethylguanidine (TMG) in acetonitrile (eq 4). Diastereomers of **5** were separated by column chromatography and then were acylated by benzoic anhydride to give **6a** and **6b**, respectively. Oxidation of **6a** and **6b** with *m*-chloroperbenzoic acid (*m*-CPBA) gave the corresponding sulfoxides **7** and sulfones **8**. The structures of these compounds were determined by ^1H NMR of **8**; the methyl protons were observed at δ 2.00 and 2.20, respectively. The former isomer can be assigned as the *u* diastereomer by analogy with the assignment of the structure of **3**. The *u* series compounds are named **6a**, **7a**, and **8a**, corresponding to the sulfide, sulfoxide, and sulfone, respectively. The *l* isomers are named **6b**, **7b**, and **8b**.



(4)

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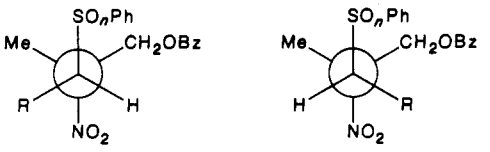
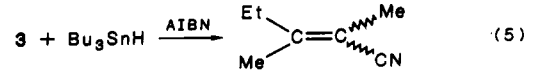


u-**6a**, *n* = 0; *u*-**7a**, *n* = 1; *u*-**8a**, *n* = 2

l-**6b**, *n* = 0; *l*-**7b**, *n* = 1; *l*-**8b**, *n* = 2

R = Me_2CH

Reductive Elimination Reactions. Reductive elimination reactions of tetrasubstituted β-nitro sulfones (**3**, **4**) were carried out by heating a mixture of β-nitro sulfones, Bu_3SnH (1.5 equiv), and azobis(isobutyronitrile) (AIBN, 0.2 equiv) in benzene at 80 °C for 2 h, resulting in clean elimination of the nitro and sulfonyl groups to give the corresponding alkenes (**9**, **10**) in good yields (eq 5 and 6).



(5)

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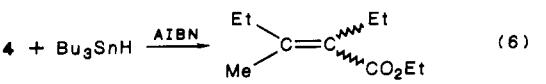


(6)

10

Other reducing agents such as Na_2S or NaTeH are also effective in inducing the reductive elimination reactions. The results are summarized in Table III.

Table III. Reductive Elimination Reaction of Compounds 3 and 4

compd	reducing agents	product	yield, %	*E*/*Z*
3a	Bu_3SnH	**9**	86	99/1
3b	Bu_3SnH	**9**	87	1/99
4a	Bu_3SmH	**10**	85	99/1
4b	Bu_3SnH	**10**	83	1/99
3a	Na_2S	**9**	76	50/50
3b	Na_2S	**9**	70	50/50
3a	NaTeH	**9**	83	63/37
3b	NaTeH	**9**	83	36/64

The most important feature in Table III is the high stereospecificity in the elimination induced by tin radicals. This specificity is lost in the elimination reaction induced by Na_2S. As compound **3a** or **4a** gives (*E*)-**9** or (*E*)-**10**,

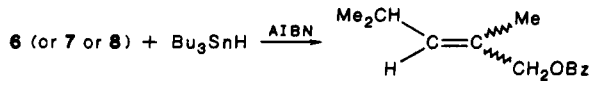
(13) Ono, N.; Tamura, R.; Nakatsuka, T.; Hayami, J.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3295.

(14) For the definition of *l* and *u*, see: Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654.

Table IV. Reductive Elimination Reactions of Compounds 6–8 with Bu_3SnH

compd	time, min	yield, %	E/Z
6a	1	80 (GLC)	75/25
6a	5	91 (GLC)	76/24
6a	10	91 (GLC)	76/24
6a	30	94 (isolated)	77/23
7a	1		90/10
7a	30		91/9
8a	1	93 (GLC)	93/7
8a	5	95 (GLC)	93/7
8a	30	88 (isolated)	96/4
6b	1	80 (GLC)	47/53
6b	5	86 (GLC)	52/48
6b	10	85 (GLC)	52/48
6b	30	80 (isolated)	52/48
7b	1		27/73
7b	5		27/73
7b	30		25/75
8b	1	80 (GLC)	15/85
8b	5	85 (GLC)	15/85
8b	30	88 (isolated)	16/84

respectively, the reaction proceeds in an anti stereospecific way. The elimination reaction of **6**, **7**, or **8** with tin radicals (eq 7) was carried out in the same way as in the elimination



(7)

11

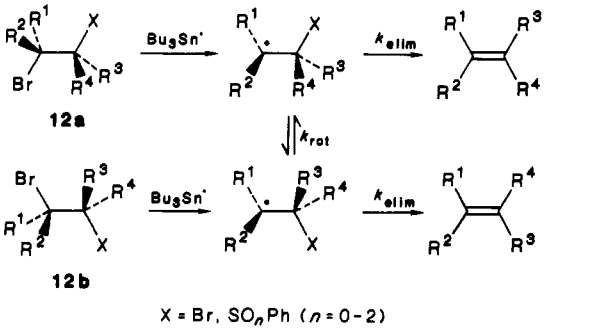
of **3** or **4**. The results are summarized in Table IV. Although tin radicals were effective in the production of **11**, other reducing agents such as Na_2S were not suitable for this reaction due to the occurrence of side reactions. Although stereospecificity in the formation of trisubstituted alkene **11** is lower than that for the formation of tetrasubstituted alkenes **9** and **10**, anti elimination is the main course in these cases, too. As the thermodynamic stability (*E*)- and (*Z*)-alkenes of tetrasubstituted alkenes is almost the same, the isomerization of these alkenes is very slow compared with trisubstituted alkenes. In fact, pure (*E*)-**9**, (*E*)-**10**, (*Z*)-**9**, or (*Z*)-**10** was isolated by the reaction of **3a**, **4a**, **3b**, or **4b** with tin radicals, respectively. On the other hand, the formation of *E*-trisubstituted alkenes is more favorable than that of *Z*-trisubstituted alkenes.

The effect of the isomerization on the *E*/*Z* values in Tables III and IV was checked. Isomerization of tetrasubstituted alkenes under the reaction conditions was not observed in elimination reactions with either tin radicals or sodium sulfide. The isomerization of **11** was not observed at 80 °C, and slow isomerization was observed at 140 °C. Thus, the effect of isomerization can be neglected in Tables III and IV.

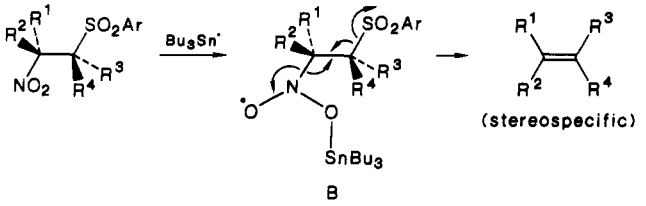
Although anti stereospecificity is well established in ionic reactions such as E_2 reactions, the stereochemistry of radical elimination is not well understood. The present elimination reaction from β-nitro sulfones is the first example in which radical elimination proceeds in an anti stereospecific way. Various substrates having two leaving groups such as compound **12** undergo the reductive elimination on treatment with tin radicals. For example, *vic*-dibromides,[15] β-bromo sulfides,[16] or β-bromo sulfoxides[17] undergo the elimination reaction with tin radicals. Stereospecificity of these elimination reactions is generally low. The reaction of β-bromo sulfones with tin radicals proceeds in a nonstereospecific way.[18] A free-radical mechanism as shown in Scheme II is presented for these reactions.[19] When k_{elim} is faster than k_{rot}, the reaction becomes stereospecific. Thus, the stereospecificity of the radical elimination reaction of **12** depends on the nature of X. The order of stereospecificity is Br > PhSO > PhS > $PhSO_2$, which is parallel to the ease of bond breaking as a radical. Evidently, the results in Tables III and IV cannot be explained by the mechanism presented in Scheme II; namely, 100% specificity in the elimination reaction from **3** or **4** suggests that the elimination proceeds via synchronous departure of tributylstannyl nitrite and tosyl radical from **3** or **4**, respectively. The order of stereospecificity in the elimination reaction from **6**, **7**, or **8** is the reverse order of the elimination reaction presented in Scheme II. β-Nitro sulfone **8** shows higher specificity than β-nitro sulfoxide **7** or β-nitro sulfide **6**. As the synchronous elimination pathway, we propose the mechanism presented in Scheme III. Tributyltin radical attacks the nitro group to form the intermediate B (tributylstannyl nitroxide radical), which undergoes synchronous bond breaking of C–N and C–S bonds by successive β-scission of radicals. Even if the bond breaking of the C–N bond is more advanced than that of the C–S bond, two bulky groups (sulfonyl and nitroxide groups) inhibit the rotation of the central C–C bond. The reductive elimination reaction induced by tin radicals proceeds via a free radical chain mechanism, for the reaction is accelerated by the presence of a catalytic amount of azobis(isobutyronitrile) (AIBN) and inhibited by the presence of a catalytic amount of *m*-dinitrobenzene (*m*-DNB). Further evidence is obtained from the reaction of β-nitroacetates with tin radicals, where alkenes are not formed and the nitro group is selectively replaced by hydrogen. This means that the sulfur groups are not ionic leaving groups but radical leaving groups.

Although the elimination by tin radicals proceeds in a stereospecific way, the reaction by sodium sulfide does not.

Scheme II



Scheme III

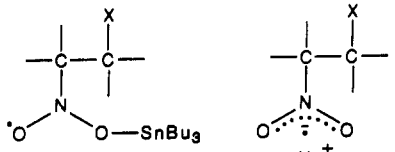


(15) Strunk, R. J.; DiGiacomo, P. M.; Aso, K.; Kuivila, H. G. *J. Am. Chem. Soc.* **1970**, *92*, 2849.
(16) Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B. *J. Am. Chem. Soc.* **1976**, *98*, 951.
(17) Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B.; Willcott, M. R., III; Inners, R. R.; Cornelis, A. *J. Am. Chem. Soc.* **1978**, *100*, 3874.
(18) Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B. *J. Org. Chem.* **1980**, *45*, 794.
(19) After elimination of X· (X = Br, SO_nAr, *n* = 0–2) in forming olefins, these radicals are the chain-carrying species by providing new tin radicals.

Table V. Reductive Elimination of *l*-17 and *u*-17.

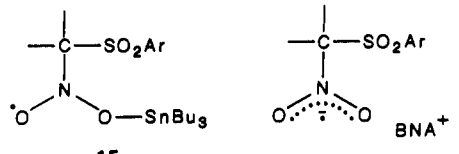
R	17	product	yield, %	*E*/*Z*
Et	*u*-17a	18a	80	89/11
Et	*l*-17a	18a	78	27/73
n-C_5H_{11}	*u*-17b	18b	82	92/8
n-C_5H_{11}	*l*-17b	18b	84	16/84
cyclohexyl	*u*-17c	18c	86	95/5
cyclohexyl	*l*-17c	18c	86	20/80

A simple explanation is that the initial products are isomerized under the conditions of sodium sulfide elimination. However, this is not true. Tetrasubstituted olefins are stable, and they are not isomerized on treatment with sodium sulfide under the same reaction conditions of the elimination. As related reactions, Kornblum reported the reductive elimination reactions from *vic*-dinitro compounds with sodium sulfide.[9] He proposed that the reaction proceeds via anion radical intermediates. He claimed that various pathways are envisioned for the loss of the second nitro group, and he had no basis for favoring any one of the possible variants. Thus, some ambiguous points remain on the mechanism of the reductive elimination with sodium sulfide. However, it can be concluded that the reaction induced by tin radicals proceeds by a different pathway from that induced by sodium sulfide, for the stereospecificity is completely different as shown in Table III. The reaction with tin radical may proceed via a nitroxide radical such as **13**, and the reaction with sodium sulfide may proceed via a loose ion radical pair such as **14**.



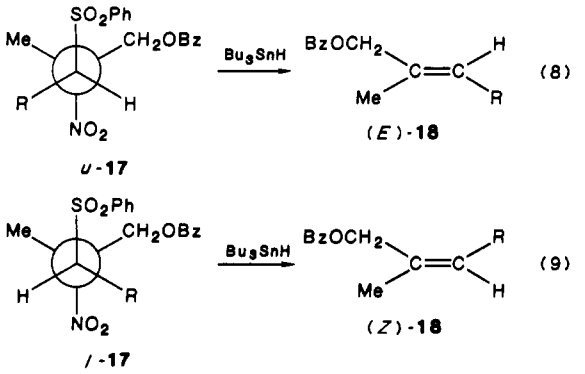
13 **14**

As the successive β-scission of radicals is more favored from **13** than **14**, the specificity is higher in the elimination induced by tin radicals than in that induced by sodium sulfide. Such different reactivity is also observed in the reaction of α-nitro sulfones;[7] namely, tin radicals are inert to α-nitro sulfones, but the sulfinate ion is readily lost on treatment of α-nitro sulfones with BNAH. This different reactivity is also explained by assuming that a nitroxide radical is formed in the latter reaction. Evidently C–S bond cleavage is possible from the intermediate **16** but is impossible from **15**.



15 **16**

The results in Table IV also support the proposed mechanism. If the stepwise mechanism is operative in the present elimination reaction, the better leaving group as a radical should give the better stereospecificity. However, the highest specificity is observed in the elimination from β-nitro sulfones. This means that the anti configuration of two bulky groups (nitro–tin complex and sulfonyl group) is the most stable as an intermediate, which undergoes the anti radical elimination. Thus, various trisubstituted olefins were prepared by the elimination of β-nitro sulfones as shown in Table V. At present, the separation of *l* and *u* isomers is necessary to get (*E*)- and (*Z*)-olefins selectively (eq 8 and 9).



(8)

(9)

In summary, the reductive elimination reactions of β-nitro sulfones induced by tin radicals proceed in an anti stereospecific way, where the cleavage of the C–N and C–S bonds proceeds synchronously. The intermediates of reductive cleavage of aliphatic nitro groups are nitroxide radicals, in which the oxygen and tin atoms are tightly bonded. Such species show different reactivities from those of anion radicals of nitro compounds, which are formed by an electron-transfer process from sodium sulfide or BNAH. The present stereospecific radical reaction may have a potential utility for organic synthesis, for most radical reactions lack stereospecificity.

Experimental Section

Infrared spectra were obtained on a Hitachi 215 spectrometer; NMR spectra were measured with a JEOL PS-100 and recorded (δ) downfield from Me_4Si. Mass spectra were recorded on a JEOL JMS-DX-300. GLC analyses were performed with a Shimadzu GC-8A with a 2-m column packed with DC-550. Elemental analyses were performed by the Kyoto University microanalysis laboratory.

Preparation of β-Nitro Sulfones 3 and 4. β-Nitro sulfones **3** and **4** were prepared according to the literature.[13]

3a: mp 129–130 °C; NMR ($CDCl_3$) δ 0.96 (t, 3 H, *J* = 8 Hz), 1.82 (s, 3 H), 2.00 (s, 3 H), 1.90–2.30 (m, 2 H), 2.48 (s, 3 H), 7.45 (d, 2 H, *J* = 8 Hz), 7.90 (d, 2 H, *J* = 8 Hz). Anal. Calcd for $C_{14}H_{18}N_2OS$: C, 54.18; H, 5.83; N, 9.03. Found: C, 53.97; H, 5.94; N, 9.00. **3b**: mp 145 °C; NMR ($CDCl_3$) δ 0.96 (t, 3 H, *J* = 8 Hz), 1.64 (s, 3 H), 1.92 (s, 3 H), 2.50 (s, 3 H), 2.60–2.90 (m, 2 H), 7.47 (d, 2 H, *J* = 8 Hz), 7.94 (d, 2 H, *J* = 8 Hz). Anal. Found: C, 54.46; H, 5.98; N, 8.72.

4a: mp 93.5–94.5 °C; NMR ($CDCl_3$) δ 0.94 (t, 3 H, *J* = 8 Hz), 1.10 (t, 3 H, *J* = 8 Hz), 1.27 (t, 3 H, *J* = 8 Hz), 1.94 (s, 3 H), 2.31 (q, 1 H, *J* = 8 Hz), 2.35 (q, 1 H, *J* = 8 Hz), 2.44 (s, 3 H), 2.40–2.50 (m, 2 H), 4.20–4.24 (m, 2 H), 7.33 (d, 2 H, *J* = 8 Hz), 7.84 (d, 2 H, *J* = 8 Hz). Anal. Calcd for $C_{17}H_{25}NO_6S$: C, 54.97; H, 6.78; N, 3.77. Found: C, 54.88; H, 6.58; N, 3.75. **4b**: mp 89–90 °C; NMR ($CDCl_3$) δ 0.77 (t, 3 H, *J* = 8 Hz), 1.01 (t, 3 H, *J* = 8 Hz), 1.23 (t, 3 H, *J* = 8 Hz), 1.94 (s, 3 H), 2.22 (q, 1 H, *J* = 8 Hz), 2.29–2.37 (m, 2 H), 2.45 (s, 3 H), 3.04 (q, 1 H, *J* = 8 Hz), 4.20–4.24 (m, 2 H), 7.32 (d, 2 H, *J* = 8 Hz), 7.84 (d, 2 H, *J* = 8 Hz). Anal. Found: C, 54.82; H, 6.85; N, 3.68.

Preparation of β-Nitro Sulfide (6). A mixture of 4-methyl-2-nitro-2-pentene (1.29 g, 10 mmol), PhSH (1.36 g, 12 mmol), 35% HCHO (1.2 g, 15 mmol), and TMG (0.04 g, 0.34 mmol) in acetonitrile (5 mL) was stirred at room temperature for 24 h. The reaction mixture was poured into water, acidified with dilute HCl, and extracted with diethyl ether. The usual workup followed by column chromatography (silica gel, hexane–ethyl acetate) gave **5**, which was separated into the *l* and *u* isomers. **5a** (or **5b**) was treated with benzoic anhydride (1 equiv) in the presence of 4-(dimethylamino)pyridine (DMAP, 0.1 equiv) to give **6a** in 83% yield.

6a: mp 66–66.5 °C; IR 1350, 1540, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (d, 3 H, *J* = 7 Hz), 1.21 (d, 3 H, *J* = 7 Hz), 1.82 (s, 3 H), 1.88–2.06 (m, 1 H), 3.94 (d, 1 H, *J* = 2 Hz), 4.50 (d, 1 H, *J* = 12 Hz), 4.88 (d, 1 H, *J* = 12 Hz), 7.20–7.62 (m, 8 Hz), 7.78–7.90 (m, 2 H). Anal. Calcd for $C_{20}H_{23}NSO_4$: C, 64.32; H, 6.21; N, 3.75. Found: C, 64.33; H, 6.26; N, 3.74. **6b**: mp 92 °C; IR 1350, 1540,

1720 cm^{-1}; NMR ($CDCl_3$) δ 1.12 (d, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 7 Hz), 1.84 (s, 3 H), 2.10–2.30 (m, 1 H), 3.89 (d, 1 H, J = 3 H), 4.78 (d, 1 H, J = 12 Hz), 4.94 (d, 1 H, J = 12 H), 7.24–7.64 (m, 8 H), 7.94–8.02 (m, 2 H). Anal. Found: C, 64.43; H, 6.23; N, 3.72.

Preparation of β-Nitro Sulfoxide (7a). To a solution of **6a** (1.31 g, 3.5 mmol) in CH_2Cl_2 (10 mL) was added a solution of *m*-CPBA (0.80 g, 3.7 mmol) in CH_2Cl_2 (30 mL) at 0 °C for 30 min. The resulting mixture was stirred at room temperature for 8 h, then poured into water, and extracted with CH_2Cl_2. The extract was washed with water and dried with anhydrous magnesium sulfate. The solvent was removed, and the residue was subjected to column chromatography (silica gel, benzene–hexane) to give **7a**: 1.28 g (94%); IR 1040, 1350, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.86 (d, J = 8 Hz, Me), 0.94 (d, J = 8 Hz, Me), 1.26 (d, J = 8 Hz, Me), 1.50 (d, J = 8 Hz, Me), 2.14–2.60 (m, 1 H, CH), 2.02 (s, 3 H), 3.54–3.70 (m, 1 H, CHSO), 4.25 (d, J = 12 Hz), 4.70 (d, J = 12 Hz), 5.00 (d, J = 2 Hz), 7.30–8.10 (m, 10 H). Anal. Calcd for $C_{20}H_{23}NSO_5$: C, 61.68; H, 5.95; N, 3.60. Found: C, 62.05; H, 5.79; N, 3.62.

Another isomer **7b** was prepared from **6b** in the same way. **7b**: mp 127–130 °C; IR 1040, 1360, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.94 (d, J = 8 Hz), 1.18 (d, J = 8 Hz), 1.38 (d, J = 8 Hz), 2.00–2.60 (m, 1 H), 1.80 (s, 1.5 H), 2.14 (s, 1.5 H), 3.60 (m, 0.5 H), 3.74 (m, 0.5 H), 4.50–4.80 (m, 1 H), 4.95 (s, 1 H), 7.30–7.94 (m, 10 H). Anal. Found: C, 61.87; H, 5.78; N, 3.68.

Preparation of β-Nitro Sulfone (8a). To a solution of **6a** (1.31 g, 3.5 mmol) in $CHCl_3$ (10 mL) was added a solution of *m*-CPBA (1.60 g, 7.4 mmol) in $CHCl_3$ (50 mL) at room temperature. The resulting solution was refluxed for 4 h. The same workup as in the preparation of **7a** gave **8a**: 1.30 g (88%); mp 130 °C; IR 1160, 1350, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.22 (d, 3 H, J = 6 Hz), 1.34 (d, 3 H, J = 8 Hz), 1.98–2.20 (m, 1 H), 2.00 (s, 3 H), 4.40 (d, 1 H, J = 1 Hz), 4.54 (d, 1 H, J = 12 Hz), 4.90 (d, 1 H, J = 12 Hz), 7.2–7.9 (m, 10 H). Anal. Calcd for $C_{20}H_{23}NSO_6$: C, 59.24; H, 5.74; N, 3.45. Found: C, 59.38; H, 5.74; N, 3.40. **8b**: mp 134 °C; IR 1160, 1350, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.18 (d, 6 H, J = 6 Hz), 2.10 (s, 3 H), 2.20 (m, 1 H), 4.64 (d, 1 H, J = 1 Hz), 4.50 (d, 1 H, J = 12 Hz), 4.76 (d, 1 H, J = 12 Hz), 7.3–8.0 (m, 10 H). Anal. Found: C, 59.44; H, 5.73; N, 3.35.

Other β-nitro sulfones (**17a–17c**) were prepared in the same way. Physical and spectral data are summarized.

u-**17a**: mp 94 °C; IR 1160, 1350, 1550, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.60 (t, 3 H, J = 8 Hz), 1.2–1.8 (m, 2 H), 1.95 (s, 3 H), 4.00 (m, 1 H), 4.98 (d, 1 H, J = 12 Hz), 5.10 (d, 1 H, J = 12 Hz), 7.3–8.0 (m, 10 H). Anal. Calcd for $C_{19}H_{21}NSO_6$: C, 58.30; H, 5.41; N, 3.58. Found: C, 58.02; H, 5.36; N, 3.36.

l-**17a**: mp 88 °C; IR 1160, 1350, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.84 (t, 3 H, J = 8 Hz), 1.50–2.25 (m, 2 H), 2.00 (s, 3 H), 4.34 (m, 1 H), 4.54 (d, 1 H, J = 12 Hz), 4.70 (d, 1 H, J = 12 Hz), 7.32–7.90 (m, 10 H). Anal. Found: C, 58.15; H, 5.33; N, 3.29.

u-**17b**: mp 80–81 °C; IR 1160, 1350, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.68 (t, 3 H, J = 8 Hz), 0.9–1.1 (m, 6 H), 1.2–1.7 (m, 2 H), 1.95 (s, 3 H), 4.00 (m, 1 H), 4.98 (d, 1 H, J = 12 Hz), 5.22 (d, 1 H, J = 12 Hz), 7.3–8.0 (m, 10 H). Anal. Calcd for $C_{22}H_{27}NSO_6$: C, 60.95; H, 6.28; N, 3.23. Found: C, 60.85; H, 6.34; N, 3.18.

l-**17b**: mp 82–83 °C; IR 1160, 1350, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.67 (t, 3 H, J = 8 Hz), 0.90–1.30 (m, 6 H), 1.4–1.8 (m, 2 H), 2.00 (s, 3 H), 4.34 (m, 1 H), 4.56 (d, 1 H, J = 12 Hz), 4.65 (d, 1 H, J = 12 Hz), 7.36–7.96 (m, 10 H). Anal. Found: C, 60.88; H, 6.34; N, 3.20.

u-**17c**: mp 144.5–145.5 °C; IR 1160, 1350, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.0 (m, 11 H), 2.00 (s, 3 H), 4.26 (s, 1 H), 4.60 (d, 1 H, J = 12 Hz), 4.92 (d, 1 H, J = 12 Hz), 7.36–7.96 (m, 10 H). Anal. Calcd for $C_{23}H_{27}NSO_6$: C, 62.00; H, 6.11; N, 3.14. Found: C, 61.65; H, 6.13; N, 2.98.

l-**17c**: mp 53–54 °C; IR 1160, 1350, 1560, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.0 (m, 11 H), 2.16 (s, 3 H), 4.58 (s, 1 H), 4.54 (d, 1 H, J = 12 Hz), 4.82 (d, 1 H, J = 12 Hz), 7.40–8.05 (m, 10 H). Anal. Found: C, 61.59; H, 6.04; N, 3.04.

Elimination of 3a with Bu_3SnH. A mixture of **3a** (0.31 g, 1 mmol), Bu_3SnH (0.44 g, 1.5 mmol), and AIBN (0.05 g, 0.3 mmol) in 2 mL of benzene was heated at 80 °C for 2 h. The reaction mixture was subjected to column chromatography (silica gel, benzene–hexane) to give (*E*)-**9**: 0.094 g (86%); IR (neat) 2250, 1640 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 8 Hz), 1.85 (s, 3 H), 2.02 (s, 3 H), 2.17 (q, 2 H, J = 8 Hz); MS, m/e (M^+) calcd for $C_7H_{11}N$ 109.0891, found 109.0891. E/Z ratio was determined to be 99/1 by GLC.

Elimination of 3b with Bu_3SnH. Compound **3b** was treated with Bu_3SnH in the same way as in the elimination of **3a**. (*Z*)-**9**: IR (neat) 2250, 1640 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (t, 3 H, J = 8 Hz), 1.83 (s, 3 H), 1.85 (s, 3 H), 2.43 (q, 2 H, J = 8 Hz); MS, m/e (M^+) found 109.0895. E/Z ratio was determined to be 1/99 by GLC.

Elimination of 3a with Na_2S. A mixture of **3a** (0.62 g, 2 mmol) and $Na_2S{\cdot}9H_2O$ (0.6 g, 2 mmol) in 3 mL of dimethylformamide was stirred at room temperature for 3 h, 15 mL of water was added, and the mixture was extracted with diethyl ether (three times). The extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated. The crude product was subjected to column chromatography (silica gel, benzene–hexane) to give **9** as a 1/1 mixture of (*E*)-**9** and (*Z*)-**9**: 0.16 g (76%); IR 2250, 1640 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (t, 1.5 H, J = 8 Hz), 1.08 (t, 1.5 H, J = 8 Hz), 1.83 (s, 1.5 H), 1.85 (s, 1.5 H), 2.02 (s, 1.5 H), 2.17 (q, 1 H, J = 8 Hz), 2.43 (q, 1 H, J = 8 Hz).

Elimination of 3b with Na_2S. Compound **3b** was treated with $Na_2S{\cdot}9H_2O$ in the same way as the elimination of **3a** to give **9**, which was the same product of elimination from **3a** with Na_2S.

Elimination of 3a with NaTeH. A solution of **3a** (0.31 g, 1 mmol) in ethanol (5 mL) was added to a solution of sodium hydrogen telluride, prepared in situ by the reaction of tellurium powder (0.64 g, 5 mmol) and $NaBH_4$ (0.45 g, 12 mmol) for 1 h in refluxing ethanol (15 mL). After the solution was stirred at room temperature for 30 min, water (25 mL) was added, and the resulting mixture was left open to air with stirring. The solution became clear after 1 h, with the decomposition of sodium hydrogen telluride. It was then filtered through Celite 545, and the filtrate was extracted with diethyl ether. After the usual workup, column chromatography (silica gel, benzene–hexane) gave **9** (0.09 g (83%)), which was analyzed by GLC; E/Z = 63/37.

Elimination of 3b with NaTeH. Compound **3b** was treated with NaTeH in the same way as the elimination of **3a**. The E/Z ratio was determined by GLC to be 36/64.

Elimination of 4a with Bu_3SnH. A mixture of **4a** (0.25 g, 0.67 mmol), Bu_3SnH (0.39 g, 1.3 mmol), and AIBN (0.05 g, 0.3 mmol) in 2 mL of benzene was refluxed for 2 h. The reaction mixture was subjected to column chromatography (silica gel, benzene–hexane) to give (*E*)-**10**, 0.10 g (85%). The E/Z ratio was determined by GLC to be 99/1: IR 1640, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 8 Hz), 1.04 (t, 3 H, J = 8 Hz), 1.32 (t, 3 H, J = 8 Hz), 1.95 (s, 3 H), 2.18 (q, 2 H, J = 8 Hz), 2.36 (q, 2 H, J = 8 Hz), 4.24 (q, 2 H, J = 8 Hz); MS, m/e (M^+) calcd for $C_{10}H_{18}O_2$ 160.1306, found 160.1302.

Elimination of 4b with Bu_3SnH. Compound **4b** was treated in the same way as in the elimination of **4a** to give (*Z*)-**10** in 83% yield: IR 1640, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 8 Hz), 1.04 (t, 3 H, J = 8 Hz), 1.47 (t, 3 H, J = 8 Hz), 1.76 (s, 3 H), 2.28 (q, 2 H, J = 8 Hz), 2.30 (q, 2 H, J = 8 Hz), 4.20 (q, 2 H, J = 8 Hz); MS, m/e (M^+) found 160.1305. The E/Z ratio was determined by GLC to be 1/99.

Elimination of 6 with Bu_3SnH. A mixture of **6a** (0.38 g, 1 mmol), Bu_3SnH (0.44 g, 1.5 mmol), and AIBN (0.05 g, 0.3 mmol) in 2 mL of benzene was heated at 80 °C for 0.5 h. The reaction mixture was subjected to column chromatography (silica gel, benzene–hexane) to give **11**, 2.04 g (94%). The E/Z ratio was determined by GLC to be 77/23. (*E*)-**11** and (*Z*)-**11** were separated by GLC and their structures were determined. (*E*)-**11**: NMR ($CDCl_3$) δ 0.99 (d, 6 H, J = 6 Hz), 1.76 (s, 3 H), 2.4–2.7 (m, 1 H), 4.70 (s, 2 H), 5.38 (d, 1 H, J = 8 Hz), 7.30–7.56 (m, 3 H), 8.00–8.12 (m, 2 H); MS, m/e (M^+) calcd for $C_{14}H_{18}O_2$ 218.1306, found 218.1282. (*Z*)-**11**: NMR ($CDCl_3$) δ 0.99 (d, 6 H, J = 6 Hz), 1.82 (s, 3 H), 2.4–2.7 (m, 1 H), 4.86 (s, 2 H), 5.30 (d, 1 H, J = 8 Hz), 7.30–7.50 (m, 3 H), 8.00–8.12 (m, 2 H); MS, m/e (M^+) found 218.1296. Elimination of **6b** was carried out in the same way to give **11** in 80% yield. The E/Z ratio was determined by GLC to be 52/48.

Elimination of 7 or 8 with Bu_3SnH. These reactions were carried out in the same way as in the elimination from **6**. The results are summarized in Table IV.

Elimination of 17 with Bu_3SnH. (*E*)-18 and (*Z*)-18 were prepared by the same procedures as in the elimination from **6**. The results are summarized in Table V.

(*E*)-**18a**: NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 8 Hz), 1.76 (s, 3 H), 2.10 (m, 2 H), 4.76 (s, 2 H), 5.58 (t, 1 H, J = 7 Hz), 7.36–7.54 (m, 3 H), 8.0–8.1 (d, 2 H, J = 8 Hz); MS, m/e (M^+) calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1190.

(*Z*)-**18a**: NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 8 Hz), 1.84 (s, 3 H), 2.10 (m, 2 H), 4.80 (s, 2 H), 5.40 (t, 1 H, J = 7 Hz), 7.36–7.54 (m, 3 H), 8.0–8.1 (d, 2 H); MS, m/e (M^+) found 204.1181.

(*E*)-**18b**: NMR ($CDCl_3$) δ 0.88 (t, 3 H, J = 8 Hz), 1.20–1.45 (m, 6 H), 1.74 (s, 3 H), 2.03 (m, 2 H), 4.76 (s, 2 H), 5.60 (t, 1 H, J = 8 Hz), 7.4–7.5 (m, 3 H), 8.0–8.1 (m, 2 H); MS, m/e (M^+) calcd for $C_{16}H_{22}O_2$ 246.1619, found 246.1618.

(*Z*)-**18b**: NMR ($CDCl_3$) δ 0.88 (t, 3 H, J = 8 Hz), 1.20–1.45 (m, 6 H), 1.84 (s, 3 H), 2.12 (m, 2 H), 4.84 (s, 2 H), 5.44 (t, 1 H, J = 8 Hz), 7.38–7.50 (m, 3 H), 7.96–8.08 (m, 2 H); MS, m/e (M^+) found 246.1620.

(*E*)-**18c**: NMR ($CDCl_3$) δ 0.90–1.80 (m, 10 H), 1.74 (s, 3 H), 2.10–2.40 (m, 1 H), 4.70 (s, 2 H), 5.37 (d, 1 H, J = 8 Hz), 7.30–7.50 (m, 3 H), 7.92–8.05 (m, 2 H); MS, m/e (M^+) calcd for $C_{17}H_{22}O_2$ 258.1620, found 258.1669.

(*Z*)-**18c**: NMR ($CDCl_3$) δ 1.0–1.8 (m, 10 H), 1.84 (s, 3 H), 2.1–2.5 (m, 1 H), 4.88 (s, 2 H), 5.30 (d, 1 H, J = 8 Hz), 7.4–7.6 (m, 3 H), 7.98–8.10 (m, 2 H); MS, m/e (M^+) found 258.1608.

Isomerization of Olefins. A mixture of (*E*)-**9** or (*Z*)-**9** (1 mmol) and 2,3-dimethyl-2,3-dinitrobutane (1 mmol) in 3 mL of dimethylformamide was stirred at room temperature for 3 h. After the usual workup, the product was analyzed by GLC. (*E*)-**9** or (*Z*)-**9** was recovered, respectively. No isomerization took place under the reaction conditions. The reaction of **6a** or **6b** with Bu_3SnH was carried out under various conditions. The E/Z ratio was determined by GLC using pentadecane as an internal standard. No isomerization was observed at 80 °C, and very slow isomerization took place at 140 °C.

Registry No. **3a**, 79424-86-5; **3b**, 79424-87-6; **4a**, 110511-65-4; **4b**, 110511-66-5; **5a**, 110511-67-6; **5b**, 110511-68-7; **6a**, 94421-38-2; **6b**, 94421-18-8; **7a**, 94482-12-9; **7b**, 94421-13-3; **8a**, 110511-69-8; **8b**, 110511-70-1; (*E*)-**9**, 67275-05-2; (*Z*)-**9**, 67275-06-3; (*E*)-**10**, 110511-73-4; (*Z*)-**10**, 110511-74-5; (*E*)-**11**, 94421-26-8; (*Z*)-**11**, 94421-27-9; *u*-**17a**, 110511-71-2; *l*-**17a**, 110529-54-9; *u*-**17b**, 110529-55-0; *l*-**17b**, 110529-56-1; *u*-**17c**, 110511-72-3; *l*-**17c**, 110529-57-2; (*E*)-**18a**, 94421-24-6; (*Z*)-**18a**, 94421-25-7; (*E*)-**18b**, 110511-75-6; (*Z*)-**18b**, 110511-76-7; (*E*)-**18c**, 110511-77-8; (*Z*)-**18c**, 110511-78-9; *m*-DNB, 99-65-0; Bu_3Sn^*, 20763-88-6; PhSH, 108-98-5; Bu_3SnH, 688-73-3; Na_2S, 1313-82-2; NaTeH, 65312-92-7; 4-methyl-2-nitro-2-pentene, 33972-68-8; 2,3-dimethyl-2,3-dinitrobutane, 3964-18-9.

Supplementary Material Available: X-ray structure (Figure 1) and tables of bond distances and angles and crystal data (Tables I and II) for compound **3a** (3 pages). Ordering information is given on any current masthead page.

Synthesis of L-(+)-Ribose via (*s*)-Pinanediol (αS)-α-Bromo Boronic Esters

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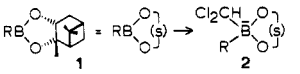
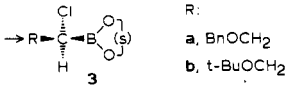
(Dibromomethyl)lithium has been tested for the chirally controlled homologation of benzyloxy-substituted boronic esters to α-halo boronic esters and found to give better yields and diastereomeric ratios than (dichloromethyl)lithium. Displacement by benzyl oxide is also more efficient with the bromides than the chlorides. (*s*)-Pinanediol [(benzyloxy)methyl]boronate (**1a**) has been converted to L-(+)-ribose (**16**) in 13% overall yield via repeated homologations and replacement of the α-bromine by benzyl oxide. The directed chiral assembly of the first four carbons is highly efficient. The low yield during connection of the fifth carbon is accompanied by boron–oxygen β-elimination and is attributed to steric hindrance.

The reaction of an (*s*)-pinanediol[1] alkylboronate **1** with (dichloromethyl)lithium inserts a carbon atom into the carbon–boron bond to form a (1*S*)-(1-chloroalkyl)boronate **3**.[2] With zinc chloride catalysis, less than 1% of the (1*R*)





isomer is formed in most cases.[3] This nearly stereospecific chiral synthesis has proved successful in the presence of ether and other functionalities and has been used for the synthesis of the insect pheromones brevicomin and eldanolide.[3] (*r*)-Pinanediol derived from (−)-α-pinene, the costlier enantiomer, was required for these pheromone syntheses.

One of the obvious applications of this chemistry would be the synthesis of carbohydrates by repetitive homologation, with replacement of the α-chlorine by benzyl oxide at each step, provided certain potential pitfalls could be avoided. Alkoxy substituents slow the rearrangement of the intermediate borate complex **2** to the point that (*s*)-pinanediol [(benzyloxy)methyl]boronate (**1a**) failed to undergo homologation to the (1*S*)-[2-(benzyloxy)-1-chloroethyl]boronate **3a** until after the discovery of the zinc chloride catalysis.[2-4] β-Elimination of boron and oxygen from β-alkoxy boronic esters should be thermodynamically highly favorable, and although it proved not to be a serious problem in the series of model compounds studied,[3] it remained a potential threat to multistep synthesis.

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