NMR Studies of Three Types of Highly Coordinated Organotin Hydrides: Chemo-, Regio-, and Stereoselective Reduction of 2,3-Epoxy Ketones

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Three types of highly coordinated organotin hydrides, Bu_2SnIH−Lewis base (Lewis bases; HMPA or tripiperidinophosphine oxide) (type A), Bu_2SnFH−HMPA (type B), and Bu_3SnH−Bu_4NX (X = F, CN) (type C), were characterized as nucleophilic, chelation, and nonchelation types of reductants, respectively, in the reaction with 2,3-epoxy ketones **1**. These reagents, which promoted a reduction of the epoxy ring and *syn*-selective and *anti*-selective carbonyl reduction, respectively, were spectroscopically confirmed with ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR and FT-IR. Furthermore, the correlations between their structures and selective reducing abilities were discussed.

Introduction

Organotin hydrides are advantageous reductants in terms of their facile availability, moderate stability, and reactivity. Many types of tin hydrides are synthesized[1] and characterized[2−4] so that they are good candidates for effective reduction of polar multiple bonds such as carbonyl groups. However, in most cases, the reductions of organohalides by tri-*n*-butyltin hydride (Bu_3SnH) have been employed under radical conditions,[2,3] and ionic reductions have not received much attention,[2,4] probably owing to moderate reactivity of ionic tin hydrides.

Facile and stable complexation with various ligands is a prevalent feature of organotin compounds,[5] which changes the structure and reactivity of original tin compounds. On the basis of this concept, we have already applied the coordinated tin compounds including organotin hydrides to organic synthesis.[6] For example, Bu_3SnH coordinated by HMPA reduces the carbonyl moiety of α-halo ketones in contrast to the halide-selective reduction by noncoordinated Bu_3SnH.[7] In addition, two types of highly coordinated tin hydrides, the Bu_2SnFH−HMPA[8] (type B) (Figure 1b) and Bu_3SnH−Bu_4NX (X = F, CN) systems[9] (type C) (Figure 1c), have been reported

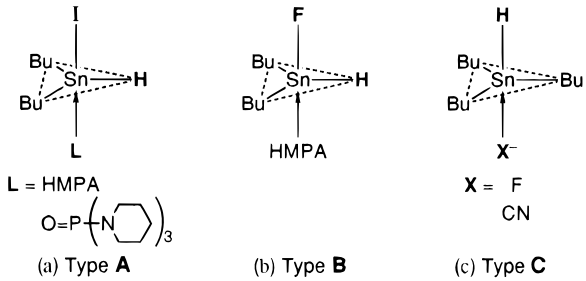

Figure 1.

to reduce the carbonyl moiety of 2,3-epoxy ketones **1** with high *anti*-[8] and *syn*-selectivities,[9c] respectively (Scheme 1).

In this paper, we report a novel tin hydride system, Bu_2SnIH−Lewis base (Lewis bases; HMPA or tripiperidinophosphine oxide) (type A) (Figure 1a). In contrast to types B and C, the type A reagents chemo- and regioselectively reduced the epoxy ring of 2,3-epoxy ketones **1** without affecting the carbonyl group to give 3-hydroxy ketones **4** (Scheme 1). This reductive selectivity presumably resulted from the activated nucleophilicity of the Sn−I bond. Furthermore, we present the

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(6) We have reported that the reactivity of organotin reagents, such as tin halides,[6a-d] tin enolates,[6e-l] and tin amides[6m-p] were enhanced by the high coordination. (a) Baba, A.; Shibata, I.; Masuda, K.; Matsuda, H. *Synthesis* **1985**, 1144−1146. (b) Shibata, I.; Baba, A.; Iwasaki, H.; Matsuda, H. *J. Org. Chem.* **1986**, *51*, 2177−2184. (c) Yano, K.; Amishiro, N.; Baba, A.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2661−2667. (d) Shibata, I.; Yoshimura, N.; Baba, A.; Matsuda, H. *Tetrahedron Lett.* **1992**, *33*, 7149−7152. (e) Baba, A.; Yasuda, M.; Yano, K.; Matsuda, H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3205−3207. (f) Shibata, I.; Nishio, M.; Baba, A.; Matsuda, H. *Chem. Lett.* **1993**, 1219−1222. (g) Shibata, I.; Nishio, M.; Baba, A.; Matsuda, H. *Chem. Lett.* **1993**, 1953−1956. (h) Shibata, I.; Nishio, M.; Baba, A.; Matsuda, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1067−1068. (i) Yasuda, M.; Oh-hata, T.; Shibata, I.; Baba, A.; Matsuda, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 859−865. (j) Shibata, I.; Baba, A. *Org. Prep. Proc. Int.* **1994**, *26*, 85−100. (k) Yasuda, M.; Kato, Y.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 4386−4392. (l) Yasuda, M.; Oh-hata, T.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1180−1186. (m) Baba, A.; Kishiki, H.; Shibata, I.; Matsuda, H. *Organometallics* **1985**, *4*, 1329−1333. (n) Shibata, I.; Toyota, M.; Baba, A.; Matsuda, H. *J. Org. Chem.* **1990**, *55*, 2487−2489. (o) Shibata, I.; Nishio, M.; Baba, A.; Matsuda, H. *J. Org. Chem.* **1992**, *57*, 6909−6914. (p) Shibata, I.; Mori, Y.; Baba, A.; Matsuda, H. *Tetrahedron Lett.* **1993**, *34*, 6567−6570.

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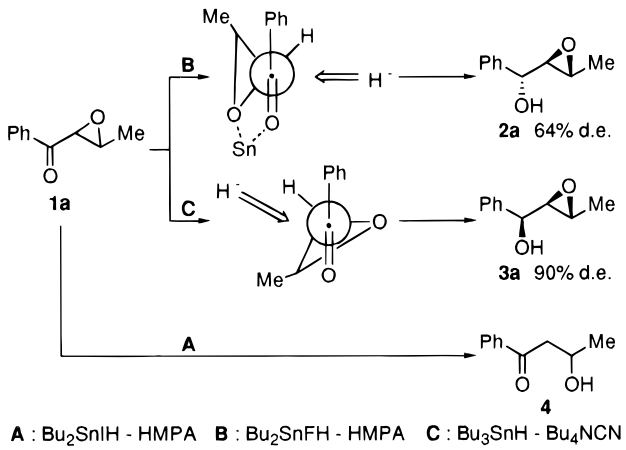
Scheme 1



A : Bu_2SnIH - HMPA **B** : Bu_2SnFH - HMPA **C** : Bu_3SnH - Bu_4NCN

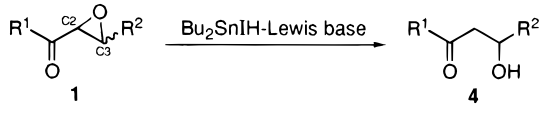
systematic spectral studies of three types of these tin hydrides (types A-C) with ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR and FT-IR and discuss the correlation between their structures and the divergent selectivities in the reduction of **1**.

Results

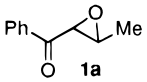
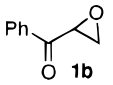
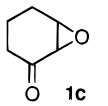
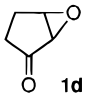
Chemoselective Reduction of Epoxides by Bu_2SnIH–Lewis Base Systems (Type A). If organotin hydride could possess a Sn–I bond, the reductive cleavage of epoxides is expected, because the efficient nucleophilic attack of iodide from the Sn–I bond to epoxy rings has already been demonstrated.[6a,b] Fortunately, Bu_2SnIH can be easily prepared by the redistribution reaction between Bu_2SnH_2 and Bu_2SnI_2.[10] We have recently found that Bu_2SnIH characteristically has quite low reducing ability for aldehydes.[11] These facts led us to expect that Bu_2SnIH species could reduce the epoxy ring of 2,3-epoxy ketones **1** in tolerance of the carbonyl group. The attempt to reduce **1c**, however, resulted in a complicated mixture including the carbonyl reduction due to a lack of nucleophilicity of the Sn–I bond in Bu_2SnIH. This problem could be resolved by high coordination of Bu_2SnIH with HMPA, which chemoselectively reduced the epoxy ring of **1c** without any side reactions (entry 4, Table 1).

As shown in Table 1, **1a** (entry 1), terminal epoxy ketone **1b** (entry 3), and bicyclic epoxy ketones **1c**,**d** (entries 4 and 5) are readily reduced to 3-hydroxy ketones **4a-d**. No products arising from the carbonyl reduction were obtained. Noteworthy is the regioselective ring cleavage at the C2–O bond. In the case of **1a**, tripiperidinophosphine oxide is a more effective ligand than HMPA (entry 2). In contrast to Bu_2SnIH–HMPA, Bu_2SnClH–HMPA[12] gave a complicated mixture in spite of the high coordination. The lower chemoselectivity of Bu_2SnClH–HMPA indicates that the selective ring cleavage is due to the nucleophilicity of the halide anion.

Table 1. Chemoselective Epoxy Reduction of 2,3-Epoxy Ketone 1 by Bu_2SnIH–Lewis Base Systems[a]

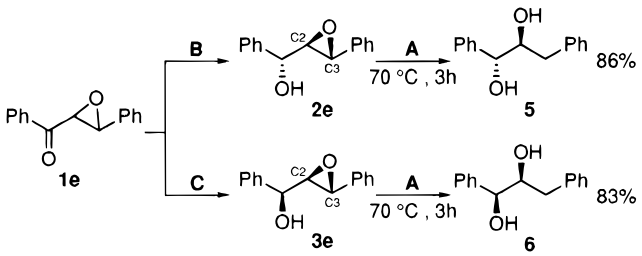


1 **4**

entry	epoxy ketone	Lewis base	conditions	yield (%)[b]
1	 **1a**	HMPA	0°C~rt , 4h	**4a**, 46
2		TPPO[c]	rt , 18h	**4a**, 58
3	 **1b**	HMPA	0°C , 1.5h	**4b**, 55
4	 **1c**	HMPA	rt , 1h	**4c**, 66[d]
5	 **1d**	HMPA	0°C , 1h	**4d**, 69[d]

[a] Epoxy ketone (**1**), 1 mmol, Bu_2SnH_2, 0.5 mmol, Bu_2SnI_2, 0.5 mmol, Lewis base, 1 mmol, THF, 1 mL. [b] Isolated yield. [c] Tripiperidinophosphine oxide. [d] GLC yield.

Scheme 2



A : Bu_2SnIH - HMPA **B** : Bu_2SnFH - HMPA **C** : Bu_3SnH - Bu_4NCN

Application to Stereocontrolled Synthesis of 1,2-Diols. The stereoselective synthesis of 1,2-diols from 2,3-epoxy ketone **1e** was demonstrated by the combined use of the three types of tin hydrides (types A-C) (Scheme 2).

At the first stage, *anti*- and *syn*-2,3-epoxy alcohols **2e** and **3e** were prepared in the reduction of **1e** with Bu_2SnFH–HMPA (type B) *via* the chelation intermediate and Bu_3SnH–Bu_4NCN (type C) *via* the nonchelation intermediate, respectively. Secondly, the isolated products, **2e** and **3e**, were further reduced by Bu_2SnIH–HMPA (type A), providing *anti*- and *syn*-1,2-diols, **5** and **6**, respectively (86% and 83% yields based on epoxy alcohols **2e** and **3e**). In contrast to the reduction of epoxy ketones **1**, the ring-opening took place at the C-3 position to hydroxy group without any side products. When $LiAlH_4$ and DIBAL-H were employed as reducing agents, in contrast to the tin hydrides, mixtures of 1,2-diol and 1,3-diol were obtained from 2,3-epoxy ketones and even from *syn*- or *anti*-2,3-epoxy alcohols.[13]

Spectroscopic Data for Bu_2SnIH–HMPA (Type A). We obtained the systematic spectral evidence for Bu_2SnIH and the highly coordinated Bu_2SnIH–HMPA, as shown in Table 2.

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(13) Epoxy ketone **1a** (1 mmol) was reduced at 0 °C by $LiAlH_4$ (2 mmol) in THF (1 mL) to give 1,2-diol (21%, *syn*:*anti* = 26:74) and 1,3-diol (30% yield, *syn*:*anti* = 13:87). DIBAL-H (1.5 mmol) in toluene furnished a complex mixture in the reduction of **1a** (1.5 mmol). Epoxy alcohol **2a** (0.5 mmol) was reduced at −78 °C by DIBAL-H (0.5 mmol) in toluene (1 mL) to give 1,2-diol (4% yield) and 1,3-dilol (5% yield). For the $LiAlH_4$ reduction of epoxy alcohols, see: Takeshita, M.; Miura, M.; Unuma, Y. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2901–2905.

Table 2. Spectral Data for Bu_2SnIH, Bu_2SnIH−HMPA and Bu_2SnFH−HMPA in THF-d_8

	Bu_2SnIH[a]	Bu_2SnIH−HMPA[b]	Bu_2SnFH−HMPA[c]
FT-IR (neat)			
ν (Sn−H) (cm^{-1})	1846.1	1857.7	1869.2
^1H NMR			
δ (Sn−^{1}H) (ppm)	6.41	7.18	7.44
^{119}Sn NMR			
δ (^{119}Sn) (ppm)	−76.3, d	−169.9, d	−123.0, d
^1J (^{119}Sn−^{1}H) (Hz)	2060	2349	2428
^1J (^{117}Sn−^{1}H) (Hz)	1968	2253	2321
^1J (Sn−$^{13}C_\alpha$) (Hz)	399 (408/390)[d]	513[e]	544(547/541)[d]

[a] 8.0 M. [b] 8.2 M. [c] 8.0 M. [d] ^{118}Sn/^{117}Sn coupling values resolved. [e] Average value; ^{119}Sn/^{117}Sn splitting was not resolved.

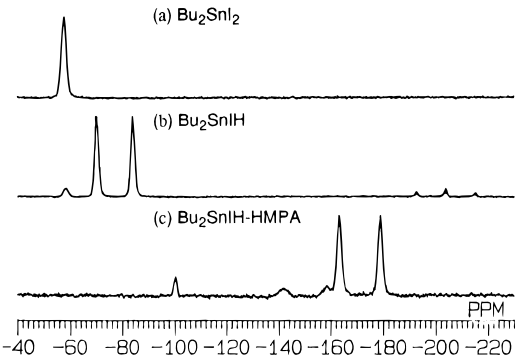

Figure 2. ^{1}H-coupled ^{119}Sn NMR spectra: (a) Bu_2SnI_2, (b) Bu_2SnI_2 + Bu_2SnH_2, (c) Bu_2SnI_2 + Bu_2SnH_2 + HMPA.

A complete transformation from Bu_2SnH_2 (−205.4 ppm) and Bu_2SnI_2 (Figure 2a) to Bu_2SnIH was confirmed with the ^{1}H-coupled ^{119}Sn NMR spectra (Figure 2 b). The addition of an equimolar amount of HMPA to the resulting Bu_2SnIH caused not only a considerable upfield shift of δ(^{119}Sn) by 93.6 ppm (Figure 2c) but also the increase of the values of ^1J(Sn−^{1}H) and ^1J(Sn−^{13}C) by 289 and 114 Hz, respectively (Table 2), indicating the rehybrization of the tin orbital from sp^3 to sp^2.[14] The coordination of the P═O group to the tin atom was also confirmed by FT-IR spectroscopic data.[15,16] These data strongly suggest the formation of a five-coordinated tin hydride with a trigonal bipyramidal geometry,[14,17] where the electronegative ligands, I and HMPA, are presumed to occupy apical positions as shown in Figure 1a.[18] In addition, the increase of the *s*-character indicates that the Sn−H bond in Bu_2SnIH−HMPA is less reactive that that in Bu_2SnIH. In FT-IR spectroscopy, an increase of ν(Sn−H) by 11.6 cm^{-1} also exhibited the inactivation of the Sn−H bond by the coordination of HMPA.

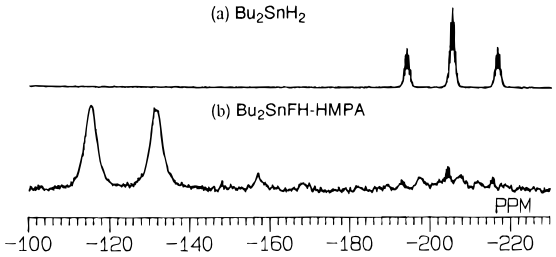

Figure 3. ^{1}H-coupled ^{119}Sn NMR spectra: (a) Bu_2SnH_2, (b) Bu_2SnF_2 + Bu_2SnH_2 + HMPA.

Spectroscopic Data for Bu_2SnFH−HMPA (Type B). The redistribution to Bu_2SnFH is difficult compared with that to Bu_2SnIH because of poor solubility of Bu_2SnF_2.[10b] We have reported that the formation of Bu_2SnFH swiftly proceeds in the presence of an equimolar amount of HMPA, providing a clear liquid (eq 1).[8]

$$Bu_2SnH_2 + Bu_2SnF_2 \underset{}{\overset{HMPA}{\rightleftharpoons}} \underset{HMPA}{2\ Bu_2SnFH} \quad \text{(eq.1)}$$

Although some spectral studies of Bu_2SnClH have been performed so far,[10b,12,19] only one example was reported concerning the ^{1}H NMR and IR spectra of Bu_2SnFH.[10b] Fortunately, we acquired the characteristic spectral data to confirm the formation of Bu_2SnFH−HMPA, summarized in Table 2 with the spectral data for Bu_2SnIH and Bu_2SnIH−HMPA. The coordination of HMPA to Bu_2SnH_2 is apparently negligible because no spectral change was observed by mixing the two (see the Experimental Section). No NMR spectral data for Bu_2SnF_2 could be obtained even by the addition of HMPA because of its insolubility.

As shown in Figure 3a, the triplet peak due to Bu_2SnH_2 appeared at −205.4 ppm in the ^{1}H-coupled ^{119}Sn NMR spectrum. In contrast, a new doublet peak was detected when Bu_2SnH_2 and Bu_2SnF_2 were mixed in the presence of HMPA (Figure 3b). At the same time, the peak due to Bu_2SnH_2 mostly disappeared. Unfortunately, the Sn−F coupling could not be detected in either ^{1}H-coupled or ^{1}H-decoupled ^{119}Sn NMR spectra because the widths at half-height are too large, 485 and 417 Hz, respectively. The presence of the fluorine atom was confirmed by the ^{19}F NMR spectrum (−163.8 ppm), although the coupling between F and Sn was not observed because of the large width at half-height (1169 Hz). In the ^{1}H NMR spectrum, the Sn−H signal due to

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(15) With HMPA, it was difficult to distinguish the P═O absorption; hence, Bu_3PO was alternatively employed. When an equimolar amount of Bu_3PO was added to Bu_2SnIH (1 mmol) in THF (3 mL), a decrease of 38.5 cm^{-1} in the P═O stretching frequency (from 1170.9 cm^{-1} to 1132.4 cm^{-1}) was observed.

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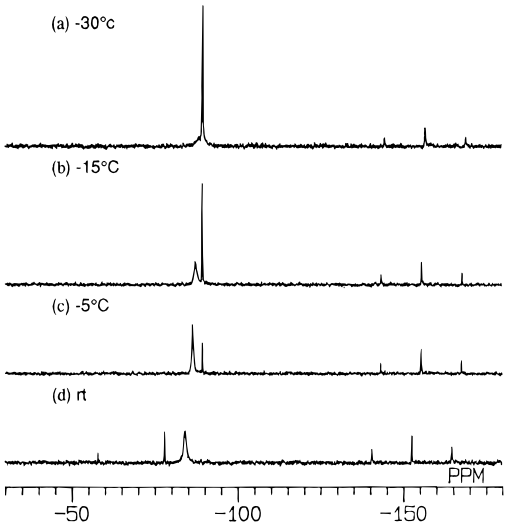


Figure 4. ^{1}H-decoupled ^{119}Sn NMR spectra of an equimolar mixture of Bu_3SnH and Bu_4NF in the presence of HMPA.

Bu_2SnFH is comprised 90% of the total Sn−H signal. These results indicate the effective formation of Bu_2SnFH.

The next problem to be resolved is whether or not HMPA coordinates to Bu_2SnFH because no spectral data of a ligand-free Bu_2SnFH can be obtained. The large coupling constant values, $^{1}J(Sn-^{1}H)$ and $^{1}J(Sn-^{13}C)$, strongly suggest the formation of a complex in comparison with those of Bu_2SnIH−HMPA. An attempt to isolate a ligand-free Bu_2SnFH was unsuccessful because removing HMPA from Bu_2SnFH−HMPA system by washing with H_2O led to white solids, corresponding to Bu_2SnF_2, and Bu_2SnH_2 as confirmed by FT-IR. This fact indicates that the redistribution shown in eq 1 is reversible and that the unstable Bu_2SnFH produced is stabilized by the coordination of HMPA. Next, we confirmed the coordination from the P═O group to the tin atom of Bu_2SnFH with FT-IR spectroscopy by employing Bu_3PO instead of HMPA. When an equimolar amount of Bu_3PO (1 mmol) was added to the mixture of Bu_2SnH_2 (0.5 mmol) and Bu_2SnF_2 (0.5 mmol) in THF (3 mL), the decrease of 42.4 cm^{-1} in the P═O stretching frequency (1170.9 to 1128.5 cm^{-1}) was observed. Such a decrease strongly suggests the coordination of the P═O group to Bu_2SnFH.[16] The above results indicate that Bu_2SnFH−HMPA is a five-coordinate tin hydride (Figure 1b).

NMR Studies of the Bu_3SnH−Bu_4NF System (Type C). Both Bu_3SnH−Bu_4NCN and Bu_3SnH−Bu_4NF afford the *syn*-selective carbonyl reduction of 2,3-epoxy ketones **1**.[20] We tried to obtain spectral evidence for the actual reducing species generated by the mixing of Bu_3SnH and Bu_4NF. The mixing of both compounds at ambient temperature caused the evolution of gas, which was further accelerated by the addition of HMPA. So, we stirred an equimolar mixture of Bu_3SnH and Bu_4NF at −78 °C in the presence of HMPA and monitored the mode of the reaction with ^{119}Sn NMR shown in Figure 4.

The peak of Bu_3SnH (−90.3 ppm) gradually decreased as the temperature was raised and completely disappeared at ambient temperature. A new peak (in the range from −84 to −88 ppm) increased gradually. Furthermore, a small peak (−157.8 ppm, triplet at −30 °C) was detected which would be assigned as $Bu_3SnF_2^-$.[21]

(20) For example, in the reduction of 2,3-epoxy ketone **1a**, Bu_3SnH−Bu_4NF provided *syn*-2,3-epoxy alcohol **3a** in 76% yield (82% de).

Unfortunately, the direct spectral evidence for the formation of a stable complex of Bu_3SnH-Bu_4NF could not be obtained. The new peak at ca. −86 ppm in ^{119}Sn NMR spectra was proved to be due to a ligand-free $Bu_3SnSnBu_3$, which was isolated from the reaction mixture after removal of Bu_4NF and HMPA.[22] The formation of $Bu_3SnSnBu_3$ supports that the reaction shown in eq 2 takes place in Bu_3SnH−Bu_4NX (X = F, CN) systems (type C).[23]

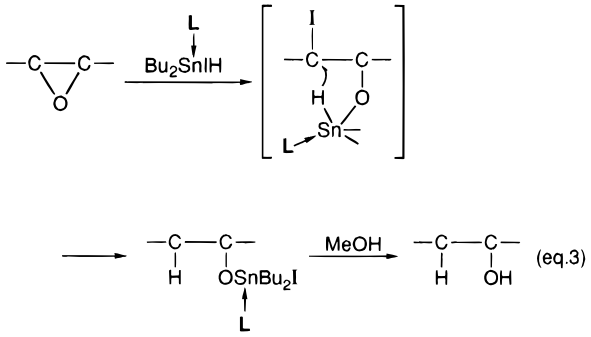
$$2\ Bu_3SnH \xrightarrow[(\ X=F,\ CN\ )]{Bu_4NX} Bu_3SnSnBu_3 + H_2\uparrow \quad \text{(eq.2)}$$

When Bu_3SnH was used alone or with HMPA, no gas evolution occurred and no peak except for the starting tin hydride was observed. Therefore, it seems reasonable that tetrabutylammonium salts greatly activate the Sn−H bond to such a degree that hydrogen gas evolves from Bu_3SnH. We presume the reactive species to be five-coordinate tin hydrides such as Figure 1c.

Discussion

NMR studies indicate that Bu_2SnIH−Lewis base complex (type A) has a trigonal bipyramidal geometry illustrated in Figure 1a. In this geometry, the nucleophilicity of iodide in the complex would be enhanced most effectively by Lewis base coordinating in a straight line. Furthermore, FT-IR spectra indicate that the nucleophilicity of hydride in Bu_2SnIH−Lewis base is decreased by the coordination of Lewis base. Both activation of the Sn−I bond and deactivation of the Sn−H bond by Lewis base probably contribute to the selective nucleophilic attack of iodide to epoxy rings prior to the carbonyl reduction by hydride.

Neither Bu_3SnH nor Bu_2SnH_2 could reduce the epoxy ring of **1c** at room temperature even in the presence of HMPA. This result indicates that the cleavage of epoxy rings by the Sn−I bond is an essential step to achieve epoxide reductions. The reaction path would be explainable as follows. At first, an iodohydrin intermediate is produced by nucleophilic attack of iodide from the Sn−I bond to the epoxy ring (eq 3).[24] Then, the resulting alkyl



iodide group is reduced by the intramolecular (or inter-

(21) The peak due to $Bu_3SnF_2^-$ at −20 °C in the Bu_3SnH−Bu_4NF (1:1) system (1.03 M with respect to tin hydride species in THF-d_8): ^{19}F NMR δ −137.4 ppm (s, $^{1}J(^{19}F-^{119}Sn)$ = 1815 Hz, $^{1}J(^{19}F-^{117}Sn)$ = 1734 Hz); ^{119}Sn NMR δ −155.6 ppm (t). For the ^{19}F and ^{119}Sn NMR spectra of $Ph_3SnF_2^-$ see: Gingras, M.; Chan, T. H.; Harpp, D. N. *J. Org. Chem.* **1990**, *55*, 2078−2090.

(22) See the Experimental Section.

(23) In addition to Bu_3SnH−Bu_4NF, the evolution of gas was observed when Bu_3SnH (3.1 mmol) was added at room temperature to a solution of Bu_4NCN (2.8 mmol) in THF-d_8 (1 mL). ^{119}Sn NMR spectrum was recorded at rt: ^{119}Sn NMR δ −84.3 (s, $^{1}J(^{119}Sn-^{119}Sn)$ = 2589 Hz, $Bu_3SnSnBu_3$).

(24) No iodohydrin intermediate could be isolated.

molecular) tin hydride moiety, providing an alcohol after quenching with MeOH.

In the reaction of 2,3-epoxy ketones **1**, the ring cleavage takes place at the C2−O bond adjacent to the C=O group to provide 3-hydroxy ketones **4**, while the nucleophilic attack to the C-3 position occurs in the reaction of 2,3-epoxy alcohols **2e** and **3e**. This change of regioselectivity can be explained only presumably in this stage. The cleavage of the latter epoxides seems to proceed *via* a general nucleophilic attack.[25] On the other hand, the cleavage of the C2−O bond of the former is due to the coordination of only the carbonyl oxygen to the tin atom because of the low acidity of Bu_2SnIH−HMPA. Predominant cleavage at the C3−O bond has been reported when both carbonyl and epoxy oxygens can coordinate to metal halides.[26]

The complex, Bu_2SnFH−HMPA (type B), is spectroscopically confirmed to be a five-coordinate tin hydride, and its structure can be inferred from that of Bu_2SnIH−HMPA (type A), as shown in Figure 1b. Although the Sn−F bond in Bu_2SnFH−HMPA may be somewhat activated by the coordination of HMPA as in type A, only the carbonyl groups of **1** to *anti*-2,3-epoxy alcohols **2** were reduced without cleavage of epoxy rings because of the inherent low nucleophilicity of fluoride.[8] The stereochemical outcome is explainable by assuming Cram's chelation model (Scheme 1).[27] In fact, when the reduction of **1e** was carried out by Bu_3SnH in the presence of $ZnCl_2$ as a representative chelating reagent, the *anti*-selective carbonyl reduction proceeded *via* Cram's chelation model (46% yield, *anti*:*syn* = 88:12). That the high Lewis acidity of the tin center in Bu_2SnFH−HMPA increased by the highly electronegative fluorine substituent is quite possibly the reason why this chelation model is taken on in spite of the coordinate disturbance by HMPA.[28]

A five-coordinated structure for Bu_3SnH−Bu_4NX (X = F, CN) (type C) is plausibly assumed as illustrated in Figure 1c. The Sn−H bond in the complex would be activated by ligands more effectively than the bonds in type A and type B since it lies in an apical position only in type C. Therefore, the type C reagent acts as a typical hydride donor to reduce the carbonyl groups of 2,3-epoxy ketones **1** to *syn*-2,3-epoxy alcohols **3** *via* the non-chelation model (Felkin−Anh model)[29] (Scheme 1).[9c] In general, a high degree of *syn*-selective carbonyl reduction of epoxy ketones **1** has not been achieved due to the difficulty of the complete removing of the coordination from epoxy oxygen to metal hydrides. The successful *syn*-selective reduction by the type C system strongly suggests the formation of an anion type of tin hydride complex like as $[Bu_3SnXH]^-[Bu_4N]^+$ (X = F, CN).

Conclusion. Systematic spectral studies of three different types (type A-C) of organotin hydrides have clarified the origins of their divergent reducing characteristics. Type A reagent, Bu_2SnIH−HMPA, acts as a nucleophilic iodide donor and reduces the epoxy ring of **1** chemo- and regioselectively. This complex is proved to have a trigonal bipyramidal geometry in which the nucleophilicity of the iodide atom in the apical position is activated most greatly by the coordination of HMPA to cleave the epoxy ring effectively. Type B reagent, Bu_2SnFH−HMPA, bears strong Lewis acidity and forms a chelate intermediate with **1** to provide *anti*-2,3-epoxy alcohols **2**. The Lewis acidity of the tin atom of type B can be increased by the electronegative fluorine substituent in spite of the coordinated disturbance by HMPA. Type C reagents, Bu_3SnH−Bu_4NX (X = F, CN), act as typical hydride donors and reduce 2,3-epoxy ketones **1** to give *syn*-2,3-epoxy alcohols **3** in excellent yields because of a "non-chelation" reduction of the carbonyl moieties by the activated Sn−H bond.

Experimental Section

Analysis. ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra were recorded at 400, 100, 376, and 149 MHz, respectively. Samples for ^1H and ^{13}C, NMR spectra of produced alcohols were examined in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Samples for ^1H, ^{13}C, and ^{119}Sn NMR spectra of tin hydrides were examined in tetrahydrofuran-d_8 containing tetramethyltin. Samples for ^{19}F NMR spectra of tin hydrides were measured relative to external fluorobenzene in tetrahydrofuran-d_8. GLC analyses were performed with a FFAP (2-m × 3-mm glass column). Column chromatography was performed by using Wakogel C-200 mesh silica gel. Preparative TLC was carried out on Wakogel B-5F silica gel. Yields were determined by ^1H NMR or GLC using internal standards.

Materials. Tri-*n*-butyltin hydride (Bu_3SnH) and di-*n*-butyltin dihydride (Bu_2SnH_2) were, respectively, prepared by the reduction of tri-*n*-butyltin chloride (Bu_3SnCl) and di-*n*-butyltin dichloride (Bu_2SnCl_2) with $LiAlH_4$.[30] Di-*n*-butyltin halide hydrides (Bu_2SnXH; X = Cl, I) were synthesized by the redistribution reaction between Bu_2SnH_2 and Bu_2SnX_2.[10a] Bu_2SnXH−HMPA (X = F, I) was synthesized by the redistribution reaction between Bu_2SnH_2 and Bu_2SnX_2 in the presence of HMPA. 2,3-Epoxy ketones **1** were prepared by the oxidation of the corresponding 2,3-unsaturated ketones using alkaline hydrogen peroxide.[31] THF was freshly distilled over sodium benzophenone ketyl, and HMPA was distilled over finely powdered calcium hydride. All reactions were carried out under dry nitrogen.

Representative Procedure for Chemoselective Reduction of Epoxide. To the solution of Bu_2SnH_2 (0.5 mmol) in 1 mL of THF were added Bu_2SnI_2 (0.5 mmol) and HMPA (1 mmol). The mixture was stirred at room temperature for 10 min. 2,3-Epoxy ketone **1** (1 mmol) was added at 0 °C, and then the solution was stirred until the Sn−H absorption (1858 cm^{-1}) disappeared in the IR spectrum. After quenching with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography, eluting with hexane−EtOAc (1:2), to give a crude product **4**. Further purification of **4** was performed by TLC, eluting with hexane−diethyl ether (1:1).

3-Hydroxy-1-phenyl-1-butanone (4a): colorless liquid; IR (neat) 3300 and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, 3H, J = 6.35 Hz), 3.05 (dd, 1H, J = 8.79 and 17.58 Hz), 3.17 (dd, 1H, J = 2.93 and 17.58 Hz), 3.35 (br, 1H), 4.37−4.45 (m, 1H), 7.44−7.96 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.39, 46.47, 63.97, 128.01, 128.64, 133.48, 136.67, 200.77; HRMS calcd for $C_{10}H_{12}O_2$ 164.0838, found 164.0831.

3-Hydroxy-1-phenyl-1-propanone (4b): colorless liquid; IR (neat) 3300 and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.22 (t, 2H, J = 5.37 Hz), 4.02 (t, 2H, J = 5.37 Hz), 7.43−7.97 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 40.36, 57.98, 127.97, 128.61, 133.44, 136.60, 200.38; HRMS calcd for $C_9H_{10}O_2$ 150.0681, found 150.0681.

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3-Hydroxy-1-cyclohexanone (4c): colorless liquid; IR (neat) 3305 and 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66−2.34 (m, 7H), 2.42 (dd, 1H, J = 7.32 and 14.16 Hz), 2.66 (dd, 1H, J = 3.91 and 14.16 Hz), 4.17−4.22 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.64, 32.79, 40.92, 50.42, 69.75, 209.95; HRMS calcd for $C_6H_{10}O_2$ 114.0681, found 114.0682.

3-Hydroxy-1-cyclopentanone (4d): colorless liquid; IR (neat) 3350 and 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.02−2.50 (m, 6H), 3.15 (br, 1H), 4.59−4.63 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 31.83, 35.48, 47.58, 69.34, 218.59; HRMS calcd for $C_5H_8O_2$ 100.0524, found 100.0502.

Stereoselective Synthesis of 1,2-Diols. To the solution of Bu_2SnF_2 (1 mmol) in 1 mL of THF was added Bu_2SnH_2 (1 mmol) and HMPA (2 mmol). The mixture was stirred at room temperature for 10 min. 1,3-Diphenyl-2,3-epoxy-1-propanone **1e** (2 mmol) was added, and the mixture was stirred until the Sn−H absorption (1869 cm^{-1}) disappeared in the IR spectrum. After the reaction was quenched with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography, eluting with hexane−EtOAc (1:1), to give an *anti*-rich mixture of alcohols **2e** and **3e** (91:9). Further purification of diastereomers was performed by TLC, eluting with hexane−diethyl ether (1:1).

A solution of Bu_4NCN (2 mmol) in THF (2 mL) was stirred at −78 °C. Bu_3SnH (2 mmol) and 1,3-diphenyl-2,3-epoxy-1-propanone **1e** (2 mmol) were added. Stirring was continued until the Sn−H absorption (1809 cm^{-1}) disappeared in the IR spectrum. After the reaction was quenched with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography, eluting with hexane−EtOAc (1:1), to give a *syn*-rich mixture of alcohols, **2e** and **3e** (14:86).

***anti*- and *syn*-1,3-Diphenyl-2,3-epoxy-1-propanol (2e and 3e):** pale yellow liquid; IR (neat) 3400 cm^{-1}; HRMS calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0999; ^1H NMR ($CDCl_3$) **2e**: δ 2.57 (d, 1H, J = 2.44 Hz), 3.28 (dd, 1H, J = 1.95 and 2.93 Hz), 4.13 (d, 1H, J = 1.95 Hz), 4.98 (dd, 1H, J = 2.44 and 2.93 Hz), 7.23−7.44 (m, 10H); **3e**: δ 2.77 (br, 1H), 3.29 (dd, 1H, J = 1.95 and 4.88 Hz), 4.00 (d, 1H, J = 1.95 Hz), 4.70 (d, 1H, J = 4.88 Hz), 7.22−7.46 (m, 10H); ^{13}C NMR ($CDCl_3$) **2e** δ 55.0, 64.9, 71.2, 125.7, 126.5, 128.3, 128.3, 128.5, 128.7, 136.5, 139.2; **3e** δ 56.9, 65.7, 73.3, 125.7, 126.2, 128.2, 128.4, 128.5, 128.7, 136.3, 140.1.

The solution of the isolated product **2e** or **3e** (1 mmol) in THF (1 mL) was added to the mixture of Bu_2SnH_2 (0.5 mmol) and Bu_2SnI_2 (0.5 mmol) in the presence of HMPA (1 mmol). Stirring was continued at 70 °C for 3 h. After the reaction was quenched with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography, eluting with hexane−EtOAc (1:1), to give a *anti*-rich or a *syn*-rich mixture of 1,2-diols, **5** (91:9) or **6** (13:87). Further purification of diastereomers was performed by TLC, eluting with hexane−diethyl ether (1:1). The stereochemistry of diastereomers was assigned by ^1H NMR in comparison with stereochemically defined authentic samples.[13]

***anti*-1,2-Dihydroxy-1,3-diphenylpropane (5):** colorless liquid, purified by TLC; IR (neat) 3300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (d, 1H, J = 3.91 Hz), 2.56 (d, 1H, J = 3.42 Hz), 2.63 (dd, 1H, J = 9.77 and 13.68 Hz), 2.72 (dd, 1H, J = 3.91 and 13.68 Hz), 4.01−4.07 (m, 1H), 4.77 (dd, 1H, J = 3.42 and 3.90 Hz); ^{13}C NMR ($CDCl_3$) δ 37.60, 76.02, 76.32, 126.47, 126.70, 127.90, 128.44, 128.54, 129.36, 138.30, 140.26; HRMS calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1131.

***syn*-1,2-Dihydroxy-1,3-diphenylpropane (6):** colorless liquid, purified by TLC; IR (neat) 3300 cm^{-1}; 1H NMR ($CDCl_3$) δ 2.51 (d, 1H, J = 3.91 Hz), 2.59 (dd, 1H, J = 8.79 and 13.67 Hz), 2.67 (dd, 1H, J = 3.91 and 13.67 Hz), 3.05 (d, 1H, J = 3.90 Hz), 3.85−3.91 (m, 1H), 4.46 (dd, 1H, J = 3.91 and 6.34 Hz); ^{13}C NMR ($CDCl_3$) δ 39.32, 76.70, 76.84, 126.41, 126.85, 128.04, 128.44, 128.50, 129.29, 1138.09, 140.90; HRMS calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1160.

^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR Studies. Chemical shifts for ^1H and ^{119}Sn NMR were measured relative to Me_4Sn. Chemical shifts for ^{13}C NMR were measured relative to THF-d_8. Chemical shifts for ^{19}F NMR were measured relative to external fluorobenzene.

Bu_2SnH_2. In a small flask, Bu_2SnH_2 (3.96 mmol) was kept under dry N_2 in 0.5 mL of THF-d_8 containing Me_4Sn; 0.8 mL of the solution was transferred to a 5 ϕ NMR tube. NMR spectra were recorded at room temperature (24 °C): ^1H NMR-(7.91 mmol in 1 mL of THF-d_8) δ 4.47 (Sn−H, $^1J(^{119}Sn-^1H)$ = 1681 Hz, $^1J(^{117}Sn-^1H)$ = 1606 Hz); ^{13}C NMR (rt) δ 7.6 ($^1J(^{119}Sn-^{13}C_\alpha)$ = 376 Hz, $^1J(^{117}Sn-^{13}C_\alpha)$ = 359 Hz), 14.3, 27.7 ($^3J(Sn-^{13}C_\gamma)$ = 58 Hz), 31.3 ($^2J(Sn-^{13}C_\beta)$ = 24 Hz); ^{119}Sn NMR (rt) δ −205.4 (t); FT-IR (neat) ν(Sn−H) = 1836.5 cm^{-1}.

Bu_2SnI_2 (8.00 mmol in 1 mL of THF-d_8); ^{119}Sn NMR (rt) δ −57.7 (s).

Bu_2SnIH (8.00 mmol in 1 mL of THF-d_8); ^1H NMR (rt) δ 6.41 (Sn−H, $^1J(^{119}Sn-^1H)$ = 2060 Hz, $^1J(^{117}Sn-^1H)$ = 1968 Hz); ^{13}C NMR (rt) δ 14.1, 17.3 ($^1J(^{119}Sn-^{13}C_\alpha)$ = 408 Hz, $^1J(^{117}Sn-^{13}C_\alpha)$ = 390 Hz), 26.7 ($^3J(Sn-^{13}C_\gamma)$ = 74 Hz), 29.7 ($^2J(Sn-^{13}C_\beta)$ = 29 Hz); ^{119}Sn NMR (rt) δ −76.3 (d); FT-IR (neat) ν(Sn−H) = 1846.1 cm^{-1}.

Bu_2SnIH−HMPA (8.17 mmol in 1 mL of THF-d_8); ^1H NMR (rt) δ 7.18 (Sn−H, $^1J(^{119}Sn-^1H)$ = 2349 Hz, $^1J(^{117}Sn-^1H)$ = 2253 Hz); ^{13}C NMR (rt) δ 14.4, 23.7 ($^1J(Sn-^{13}C_\alpha)$ = 513 Hz), 27.1 ($^3J(Sn-^{13}C_\gamma)$ = 84 Hz), 29.5; ^{119}Sn NMR (rt) δ −169.9 (d); FT-IR (neat) ν(Sn−H) = 1857.7 cm^{-1}.

Bu_2SnH_2−HMPA (8.34 mmol in 1 mL of THF-d_8); ^1H NMR (rt) δ 4.46 (Sn−H, $^1J(^{119}Sn-^1H)$ = 1670 Hz, $^1J(^{117}Sn-^1H)$ = 1596 Hz); ^{13}C NMR (rt) δ 7.7 ($^1J(^{119}Sn-^{13}C_\alpha)$ = 378 Hz, $^1J(^{117}Sn-^{13}C_\alpha)$ = 361 Hz), 14.3, 27.7 ($^3J(Sn-^{13}C_\gamma)$ = 57 Hz), 31.3 ($^2J(Sn-^{13}C_\beta)$ = 24 Hz); ^{119}Sn NMR (rt) δ −204.5 (t); FT-IR (neat) ν(Sn−H) = 1836.5 cm^{-1}.

Bu_2SnFH−HMPA (7.96 mmol in 1 mL of THF-d_8); ^1H NMR (rt) δ 7.44 (Sn−H, $^1J(^{119}Sn-^1H)$ = 2428 Hz, $^1J(^{117}Sn-^1H)$ = 2321 Hz, $w_{1/2}$ = 4.4 Hz); ^{13}C NMR (rt) δ 14.4, 19.8 ($^1J(^{119}Sn-^{13}C_\alpha)$ = 547 Hz, $^1J(^{117}Sn-^{13}C_\alpha)$ = 541 Hz), 27.7 ($^3J(Sn-^{13}C_\gamma)$ = 82 Hz), 28.9 ($^2J(Sn-^{13}C_\beta)$ = 29 Hz); ^{119}Sn NMR (rt) δ −123.0 (d, $w_{1/2}$ = 485 Hz); ^{19}F NMR (3.99 mmol in 1 mL of THF-d_8, rt) δ −163.8 (br, $w_{1/2}$ = 1169 Hz); FT-IR (neat) ν(Sn−H) = 1869.2 cm^{-1}.

Bu_3SnH (5.98 mmol in 1 mL of THF-d_8); ^1H NMR (rt) δ 4.772 (1H, $^1J(^{119}Sn-^1H)$ = 1594 Hz $^1J(^{117}Sn-^1H)$ = 1524 Hz, Sn−H); ^{119}Sn NMR δ −90.3 (d, $^1J(^{119}Sn-^1H)$ = 1595 Hz).

Bu_3SnH−Bu_4NF. To a solution of Bu_4NF (1.00 mmol) in THF-d_8 (1 mL) was added Bu_3SnH (1.07 mmol) at −78 °C in the presence of HMPA (2.01 mmol). NMR spectra were recorded at variable temperatures: ^{119}Sn NMR (−30 °C) δ −88.5 (s), −89.6 (d, $^1J(^{119}Sn-^1H)$ = 1565 Hz), −157.3 (t, $^1J(^{119}Sn-^{19}F)$ = 1826 Hz); ^{119}Sn NMR (−15 °C) δ −87.3 (s), −89.5 (d, $^1J(^{119}Sn-^1H)$ = 1568 Hz), −156.8 (t, $^1J(^{119}Sn-^{19}F)$ = 1816 Hz); ^{119}Sn NMR (−5 °C) δ −86.4 (s), −89.4 (d, $^1J(^{119}Sn-^1H)$ = 1624 Hz), −155.4 (t, $^1J(^{119}Sn-^{19}F)$ = 1815 Hz); ^{119}Sn NMR (rt) δ −84.1 (s), −152.7 (t, $^1J(^{119}Sn-^{19}F)$ = 1799 Hz).

$Bu_3SnSnBu_3$. The NMR spectrum of a THF-d_8 solution of ca. 1 mmol of $Bu_3SnSnBu_3$ isolated from the mixture of Bu_3SnH−Bu_4NF and HMPA was recorded at rt: ^{119}Sn NMR δ −84.4 (s, $^1J(^{119}Sn-^{119}Sn)$ = 2574 Hz); HRMS calcd for $C_{24}H_{53}Sn_2$ 582.2272, found 582.2263. Commercially available $Bu_3SnSnBu_3$ (8.07 mmol in 1 mL of THF-d_8); ^{119}Sn NMR (rt) δ −84.2 (s, $^1J(^{119}Sn-^{119}Sn)$ = 2589 Hz).

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra of **2e**, **3e**, **4a-d**, **5**, and **6** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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