$HO_2^{2-} \rightarrow Cu^{2+}$ CT is observed at higher energies (340–500 nm)[17] due to the strong bonding interaction of the proton with the peroxide π^* orbital. The fact that the reduced type 3 site in T2D does not react with dioxygen[4,18] indicates a major role for the type 2 site in catalysis, and we propose that a μ-1,1 hydroperoxide bridges one of the oxidized type 3 and the reduced type 2 coppers in the laccase oxygen intermediate (Scheme I, left). A type 2–type 3 bridging mode has been defined by low-temperature MCD studies of N_3^- binding to the fully oxidized trinuclear copper site.[2]

In contrast to hemocyanin (Scheme I, right), protonation of the bound peroxide in laccase is expected to lead to irreversible binding and promote further reduction to water. Furthermore, we have observed that exogenous ligands bridge mixed valent (Cu^{2+}–Cu^{1+}) binuclear sites with an unusually high affinity,[19] suggesting that bridging to the reduced type 2 copper stabilizes the oxygen intermediate in T1Hg laccase. An attractive feature of this model is that μ-1,1 hydroperoxide cobalt complexes[20] have been demonstrated to be most reactive in further reduction to water.[21]

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Stereochemical Studies on Chiral, Nonconjugated, Nitrogen-Substituted Carbanions Generated by Tin–Lithium Exchange

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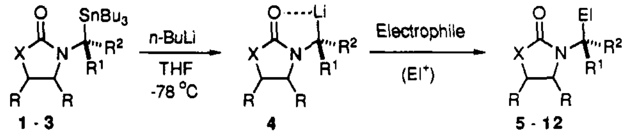
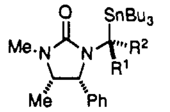
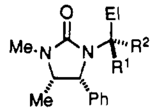
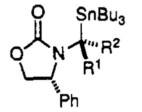
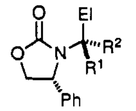
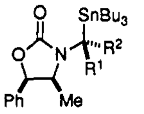
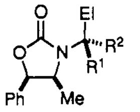
Nitrogen-substituted carbanions have been widely studied and have become useful intermediates for the synthesis of amines and their derivatives.[1] Chiral, conjugated versions of these carbanions have seen considerable research activity.[2-5] While several stereochemical studies have been reported on racemic, nonconjugated anions,[6-11] Walborsky[12] and Gawley[4c] have published the only examples of chiral, *nonracemic*, nonconjugated, nitrogen-substituted carbanions. Both cases involve cyclic systems, where small-ring strain[12,13] or conformational considerations[4c] affect the configuration of the carbanion. The configurational stability of acyclic nitrogen-substituted carbanions has not been studied, and there have been no reports on the generation of chiral, nonracemic,

Table I. Reactions of Chiral Nitrogen-Substituted Carbanions Generated by Tin–Lithium Exchange



a: R^1=Me, R^2=H **b**: R^1=H, R^2=Me **c**: R^1=Et, R^2=H **d**: R^1=H, R^2=Et **e**: R^1=iPr, R^2=H

Entry	Stannane	Electrophile	Product(s)	El	Ratio[a]	Yield (%)[b]
						
1	**1a**	DCl/D_2O	**5a**	D	–	63
2	**1c**	DCl/D_2O	**5c**	D	–	72
3	**1e**	DCl/D_2O	**5e**	D	–	82
4	**1a**	Bu_3SnCl	**1a**	$SnBu_3$	–	46
5	**1b**	Bu_3SnCl	**1a** + **1b**	$SnBu_3$	1:2.4[c]	44
6	**1a**	Bu_3SnCl/TMEDA	**1a**	$SnBu_3$	–	48
7	**1b**	Bu_3SnCl/TMEDA	**1a**	$SnBu_3$	–	48
8	**1c**	Bu_3SnCl	**1c**	$SnBu_3$	–	62
9	**1e**	Bu_3SnCl	**1e**	$SnBu_3$	–	67
10	**1c**	cyclohexanone	**6c**	$C(OH)(CH_2)_5$	–	78
11	**1c**	PhCHO	**7c**	CH(OH)Ph	1.7:1[d]	88
12	**1c**	iPrCHO	**8c**	CH(OH)iPr	1.5:1[d]	91
13	**1c**	$ClCO_2Et$	**9c** + **9d**	CO_2Et	12:1	83
						
14	**2a**	PhCHO	**10a**	CH(OH)Ph	1:1[d]	69
15	**2b**	PhCHO	**10a**	CH(OH)Ph	1:1[d]	76
						
16	**3a**	Bu_3SnCl	**3b**	$SnBu_3$	–	52
17	**3b**	Bu_3SnCl	**3b**	$SnBu_3$	–	76
18	**3a**	PhCHO	**11b**	CH(OH)Ph	1:1[d]	50
19	**3b**	PhCHO	**11b**	CH(OH)Ph	1:1[d]	82
20	**3a**	cyclohexanone	**12b**	$C(OH)(CH_2)_5$	–	39
21	**3b**	cyclohexanone	**12b**	$C(OH)(CH_2)_5$	–	32

[a] A dash (–) indicates that only one product was detected by 300-MHz ^1H NMR. [b] Yields of isolated, purified materials. [c] Ratio after 15 min at −78 °C. See Figure 1 for ratios at other times. [d] Mixture of erythro and threo isomers, which were not assigned.

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(13) Seebach has studied a chiral, nonracemic, configurationally stable 2-lithioaziridine.[5] Even though the anion is substituted by a thioester, the small ring prevents epimerization.

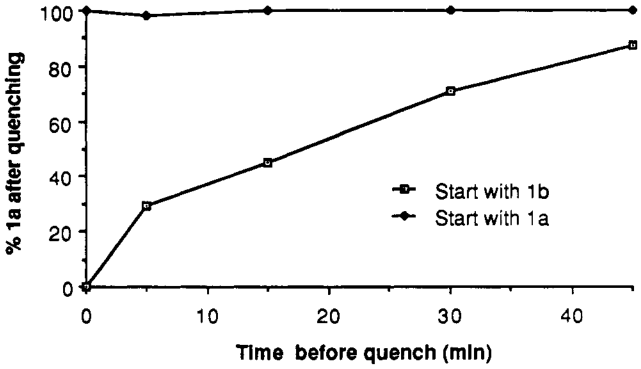

Figure 1. Results of tin–lithium exchange on stannanes **1a** and **1b** after Bu$_3$SnCl quench.

acyclic, nonconjugated anions, although closely related acyclic benzylic anions have been recently studied by Gawley.[4a] We report that the tin–lithium exchange method allows the generation of such carbanions, which undergo highly stereoselective reactions with electrophiles. Evidence for configurational stability was obtained.

We recently reported that nonconjugated (racemic or achiral), dipole-stabilized, nitrogen-substituted carbanions could be generated from α-amino stannane derivatives by tin–lithium exchange, allowing access to primary amines after reaction with electrophiles and deprotection.[14,15] We now report the transmetalation of chiral stannanes **1–3** and the stereoselective reactions of the resultant anions **4**.

Stannanes **1–3** were prepared by two routes. Alkylation of chiral heterocycles[16-20] (NaH, DMF, (1-iodoethyl)tributylstannane[14,21]) gave stannanes **1a,b** (1:1, 33%), **2a,b** (1:1, 89%), and **3a,b** (1:1, 42%), which were separable by chromatography. A new and highly stereoselective approach to chiral α-amino stannane derivatives **1a**, **1c**, and **1e** was also developed, which relies on the displacement of *N*-[1-(*p*-tolylsulfonyl)alkyl]imidazolidinones with (tributylstannyl)lithium.[22]

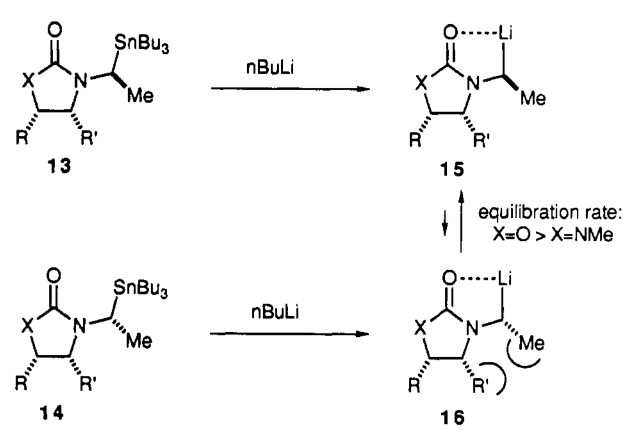

Figure 2. Proposed equilibration of anions.

Transmetalation of the chiral stannanes **1–3** with *n*-BuLi at −78 °C in THF followed by quenching with various electrophiles proceeded with high stereoselectivity at the carbanionic center (Table I). Evidence for the stereochemical assignment of the products was obtained by quenching the anions with Bu$_3$SnCl, since the products may be correlated with the known structures of the starting stannanes.[22] Transmetalation of **1a** followed by quenching with Bu$_3$SnCl afforded only **1a**, with no evidence for the formation of diastereomer **1b** (entry 4). Side-by-side control reactions which were quenched with acetic acid showed that transmetalation was complete within 5 min at −78 °C. Therefore, **1a** cannot be a result of incomplete transmetalation. Transmetalation of stannane **1b** (epimeric with **1a**) followed by quenching with Bu$_3$SnCl after 15 min gave a 2.4:1 ratio of **1b** to **1a** (entry 5). Again, control experiments showed that transmetalation was complete before adding Bu$_3$SnCl. The transmetalation of **1b** was studied in greater detail by allowing the anion to stir for longer periods of time before addition of Bu$_3$SnCl, which showed that **1a** eventually became the major product (Figure 1). A similar transmetalation study starting with **1a** showed that stereoisomer **1a** was always isolated, regardless of the elapsed time before quenching with Bu$_3$SnCl. Convergence of the two curves in Figure 1 could not be realized, since anion decomposition limited the time scale of these experiments. As shown in Figure 2, transmetalation of the two diastereomeric stannanes **13** (e.g., **1a**) and **14** (e.g., **1b**) occurs with retention of configuration[23] and leads initially to anions **15** and **16**, which may equilibrate over time to **15**, the most stable anion.[24] The anion **15** then reacts with

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(17) For the use of carbamates in the formation of dipole-stabilized carbanions, see refs 4a, 9a, 14, and the following: (a) Seebach, D.; Hassel, T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 274. (b) Armande, J. C.; Pandit, U. K. *Tetrahedron Lett.* **1977**, 897. (c) Macdonald, T. L.; Narayanan, B. A. *J. Chem. Res., Synop.* **1983**, *48*, 1129. (d) Macdonald, T. L. *J. Org. Chem.* **1980**, *45*, 193. (e) Comins, D. L.; Weglarz, M. A. *J. Org. Chem.* **1988**, *52*, 4437. (f) Comins, D. L.; LaMungon, P. H. *Tetrahedron Lett.* **1989**, *30*, 5053–5056. (g) Beak, P.; Lee, W.-K. *Tetrahedron Lett.* **1989**, *30*, 1197–1200. (h) For the transmetalation of stannanes in the presence of a more remote carbamate substituent, see: Zidani, A.; Vaultier, M. *Tetrahedron Lett.* **1986**, *27*, 857–860.

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(22) This route is similar in concept to existing methods for the preparation of α-amino stannanes from iminium ions or their precursors.[15] Condensation of (4*R*,5*S*)-1,5-dimethyl-4-phenylimidazolidin-2-one[18] with aldehydes in the presence of *p*-toluenesulfinic acid[22a,b] gave crystalline (4*R*,5*S*,1′*S*)-1,5-dimethyl-3-[1-(*p*-tolylsulfonyl)alkyl]-4-phenylimidazolidin-2-ones as single stereoisomers (X-ray). Displacement of these sulfones with Bu$_3$SnLi proceeded with complete retention of configuration.[22c,d] The stereochemistry of the stannanes **1a**, **1c**, and **1e** was based on X-ray crystallographic determination of the structure of **1c**. The details of this chemistry, including mechanistic studies and application to other stannanes, will be included in the full account of this work. (a) Engberts, J. B. F. N.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 942–950. (b) Engberts, J. B. F. N.; Olijnsma, T.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 1211–1222. (c) For the reactions of similar sulfones with carbon nucleophiles, see: Brown, D. S.; Hansson, T.; Ley, S. V. *Synlett* **1990**, 48–49 and references therein. While this work was in progress, a similar method was used by Quayle to prepare 4-(tributylstannyl)azetidin-2-ones: (d) MacLeod, C.; Quayle, P.; Davies, G. M. *Tetrahedron Lett.* **1990**, *31*, 4927–4930.

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electrophiles with retention of configuration. While evidence for the equilibration of other heteroatom-substituted carbanions has been reported previously,[4,5,12,13,23d,25] this study is unique in that a simple alkyl-substituted, acyclic, nitrogen-substituted carbanion shows an observable barrier to inversion. When the transmetalation of **1b** was carried out with TMEDA present, no evidence for configurational stability was observed, and only **1a** was produced after quenching with Bu_3SnCl (entry 7). The ligating ability of TMEDA may disrupt the chelate **16**, allowing a more rapid equilibration to **15**.

The use of carbonyl compounds as electrophiles led to the efficient and stereoselective formation of β-amino alcohol derivatives (entries 10–12) and an α-amino ester derivative (entry 13). The stereochemistry of compounds **6c–9d** was based on the assumption that carbonyl addition occurred with retention of configuration. When aldehydes were used, two of the four possible stereoisomers were formed, presumably via high stereoselectivity with respect to the carbanion coupled with modest facial selectivity with respect to the aldehyde.[26]

Oxazolidinones were also useful in achieving high levels of stereoselection (entries 14–21). However, no evidence for the configurational stability of the anion derived from **3a** was obtained (entry 16). Quenching with Bu_3SnCl after 5 min produced only **3b**. Evidently, the equilibration of **16** to **15** is faster in the oxazolidinone series (Figure 2, visualize enantiomers of all structures), perhaps due to the poorer lithium-ligating ability of a carbamate carbonyl oxygen versus a urea carbonyl oxygen. A higher energy chelate would be expected to allow easier inversion since the chelate is probably temporarily disrupted by inversion. The stereochemical outcome of these reactions is also consistent with recent work by Gawley, who studied acyclic benzylic anions derived from the deprotonation of chiral *N*-benzyloxazolidinones.[4a]

In summary, chiral, nonracemic α-amino stannane derivatives were prepared, and these stannanes were effective precursors to chiral nitrogen-substituted carbanions, which underwent stereoselective reactions with electrophiles. Evidence for configurational stability was found for these nonconjugated, acyclic anions, with the barrier to inversion being a function of the substrate and reaction conditions. Studies on the use of these chiral, nonracemic anions for the synthesis of optically pure nitrogen-containing molecules are underway and will be reported in due course.

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Supplementary Material Available: Representative experimental procedures and spectral data for all new compounds and a procedure for making the chiral stannanes by displacement of sulfones with Bu_3SnLi (7 pages). Ordering information is given on any current masthead page.

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(24) Semiempirical MNDO calculations[24a] were carried out with MOPAC[24b] on ether-solvated diastereomeric anions **15** and **16** derived from **1a** and **1b**, respectively, and showed that **15** was more stable by 1.44 kcal/mol. Details will be presented in the full account of this work. (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907. (b) Stewart, J. J. P. Quantum Chemistry Program Exchange, No. 455, Version 6.0. For other studies on the theoretical and experimental structures of similar anions, see refs 4a,b and the following: (c) Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 4108–4110. (d) Bach, R. D.; Braden, M. L.; Wolber, G. J. *J. Org. Chem.* **1983**, *48*, 1509–1514. (e) Bartolotti, L. J.; Gawley, R. E. *J. Org. Chem.* **1989**, *54*, 2980–2982. (f) Seebach, D.; Hansen, J.; Seiler, P.; Gromek, J. M. *J. Organomet. Chem.* **1985**, *285*, 1–13.

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(26) Previous observations on the addition of nitrogen-substituted carbanions to aldehydes show that the erythro/threo selectivities vary widely.[1,2,4–6,9–11,14]

Tractable Silicon-Containing Poly(diphenylacetylenes): Their Synthesis and High Gas Permeability

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Silicon-containing polyacetylenes tend to exhibit high gas permeability, and poly[1-(trimethylsilyl)-1-propyne] [poly(**1**)], one of those polymers, shows extremely high oxygen permeability.[1] Though poly(diphenylacetylene)[3] [poly(**2**)] is, to our knowledge, thermally the most stable polyacetylene,[4] it is insoluble in any solvent.[5] We anticipated that introduction of the trimethylsilyl group into poly(**2**) might provide soluble, highly gas permeable polymers. This communication reports on the polymerization of 1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene (*p*-**3**) and 1-phenyl-2-[*m*-(trimethylsilyl)phenyl]acetylene (*m*-**3**) by $TaCl_5$-based catalysts and polymer properties.[6] The product polymers, poly(*p*-**3**) and poly(*m*-**3**), possess high molecular weights over 1×10^6, dissolve in various organic solvents, are thermally appreciably stable, and show very high gas permeability.

Polymerizations[8] of *p*-**3** and *m*-**3** were carried out using $TaCl_5$–cocatalyst systems, which are effective in the polymerization of **2**, under dry nitrogen by the method described before.[3] The monomers were consumed virtually quantitatively in the presence of $TaCl_5$–*n*-Bu_4Sn (1:2) and $TaCl_5$–Et_3SiH (1:2) catalysts to give methanol-insoluble polymers in over 70% yields (Table I). As was expected, the produced polymers totally dissolved in various organic solvents such as toluene and $CHCl_3$. The weight-average molecular weights ($\bar{M}_w$) based on gel permeation chromatography (GPC)[10] were as high as $\sim 2 \times 10^6$ with poly(*p*-**3**) and $\geq 1 \times 10^6$ with poly(*m*-**3**). The methanol-soluble byproducts were linear oligomers according to GPC and NMR. The polymerizations of *p*-**3** and *m*-**3** by $TaCl_5$–*n*-Bu_4Sn proceeded without induction phases and were completed in 15 and 90 min, respectively, under the conditions of Table I. In contrast, no polymers were formed with $TaCl_5$ alone.

From elemental analyses and NMR and IR spectra, it is concluded that the polymers obtained possess alternating double bonds along the main chain.[11] The present polymers showed UV

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(1) (a) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473–7474. (b) Takada, K.; Matsuya, H.; Masuda, T.; Higashimura, T. *J. Appl. Polym. Sci.* **1985**, *30*, 1605–1616. (c) Ichiraku, Y.; Stern, Y. A.; Nakagawa, T. *J. Membr. Sci.* **1987**, *34*, 5–18. (d) Masuda, T.; Iguchi, Y.; Tang, B.-Z.; Higashimura, T. *Polymer* **1988**, *29*, 2041–2049. (e) Langsam, M.; Robeson, L. M. *Polym. Eng. Sci.* **1988**, *29*, 44–54. Poly(**1**) possesses some disadvantages such as low permselectivity and time dependence of gas permeability; improvements have been attempted.[2]

(2) (a) Langsam, M.; Anand, M.; Karawacki, E. J. *Gas Sep. Purif.* **1988**, *2*, 162–170. (b) Nakagawa, T.; Saito, T.; Asakawa, S.; Saito, Y. *Gas Sep. Purif.* **1988**, *2*, 3–8. (c) Nagase, Y.; Ueda, T.; Matsui, K.; Uchikura, M. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 171–179.

(3) Niki, A.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1553–1562.

(4) According to thermogravimetric analysis (TGA; heating rate 10 °C/min), the temperature at which the weight loss of poly(**2**) starts in air is ~500 °C.[3]

(5) In general, high molecular weight polymers from symmetrically disubstituted acetylenes [e.g., poly(4-octyne)] are insoluble in any solvent.[9c]

(6) The monomers were prepared with reference to the method of T.-L. Chang et al.;[7] i.e., phenylacetylene was reacted with bromoiodobenzenes in the presence of $(PPh_3)_2PdCl_2$, and the products were lithiated with *n*-BuLi followed by reaction with $ClSiMe_3$.

(7) Chang, T.-L.; Holzknecht, L. J.; Mark, H. B., Jr.; Ridgway, T. H.; Zimmer, H. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 989–997.

(8) The polymerization of substituted acetylenes by group 5 and 6 transition-metal catalysts is considered to proceed via metal carbenes like the ring-opening polymerization of cycloolefins,[9a,b] because identical catalysts are effective and many common features are observed in both polymerizations.[9c]

(9) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 165–172. (b) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907–915. (c) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 121–165.

(10) GPC curves were observed on a Shimadzu LC-9A liquid chromatograph (eluent $CHCl_3$, Shodex A805, A806, and A807 polystyrene gel columns). A polystyrene calibration was used to calculate $\bar{M}_w$ and $\bar{M}_n$.

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