dride[14] would lead to enhanced selectivity in the silane reduction. These results show that steric hindrance from the hydrogen atom source can effect the stereoselectivity of atom transfer to alkenyl radicals in the same way that steric hindrance on the radical itself alters the stereoselectivity.[11]

Thus, it has been shown that steric requirements in the transition state for radical cyclization reactions can be exploited to control the stereoselectivity of exocyclic alkene formation[15] and that by judicious choice of reaction temperature and reducing agent high stereoselectivity for either the *E*- or the *Z*-isomer can be obtained. This represents one of the first examples of control of olefin stereochemistry in a radical cyclization by the reducing agent. Investigations of the scope and limitations of this methodology are continuing, and the results of these studies will be presented in due course.

Acknowledgment. We thank the Natural Science and Engineering Research Council (NSERC) of Canada for financial support of this work.

Supplementary Material Available: Experimental procedures, compound characterization data, and spectra (31 pages). This material is contained in many 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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Tin(II) Amides: New Reagents for the Conversion of Esters to Amides

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Summary: Mixed tin(II) amides are generated, in situ, via addition of aliphatic amines to $\mathrm{Sn[N(TMS)_2]_2}$. Condensation of these reagents with esters yields amides.

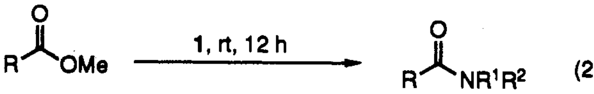
Tin(II) amides provide a convenient source of nucleophilic amines. Recently, we reported the utility of these reagents for the chemo- and stereoselective synthesis of enamines from aldehydes.[1] We now describe a facile, in situ procedure for the generation of tin(II) amides, and their subsequent application for the conversion of esters to amides.

Bis[bis(trimethylsilyl)amido]tin(II), $\mathrm{Sn[N(TMS)_2]_2}$, is readily obtained from the reaction of $\mathrm{SnCl_2}$ with $\mathrm{LiN(TMS)_2}$.[2] We previously demonstrated that this silyl amide reacts chemoselectively with primary aldehydes, to the exclusion of secondary aldehydes, ketones, and esters, to give *N,N*-bis(trimethylsilyl) enamines. We also found that tin(II) amides prepared from dialkylamines were more reactive than silyl amides and converted both aldehydes and ketones to enamines. In this paper, we describe a new procedure for preparing tin(II) amides and their utility for the direct conversion of esters to amides.[3,4]

When a solution of $\mathrm{Sn[N(TMS)_2]_2}$ in hexane is treated with 1 equiv of a primary or secondary aliphatic amine, a mixed tin(II) amide is generated via a metathesis reaction (eq 1).[5,6] The hexamethyldisilazane that is liberated in

$$\mathrm{Sn[N(TMS)_2]_2} \xrightarrow[\text{- HN(TMS)}_2]{\mathrm{HNR^1R^2},\ \text{hexane}} \underset{\mathbf{1}}{\left[\,\mathrm{(TMS)_2N\text{-}Sn\text{-}NR^1R^2}\,\right]} \qquad (1)$$

this process does not interfere with any further condensations of the tin(II) amide and need not be removed. Subsequent reaction of an ester with this mixed tin(II) amide results in formation of an amide *via transfer of the aliphatic amine* (eq 2 and Table I). In all cases we have


(2)

examined, the bis(trimethylsilyl)amino group serves as a nontransferrable ligand.[7]

The following procedure is representative: to a hexane solution of $\mathrm{Sn[N(TMS)_2]_2}$ (0.53 g, 1.2 mmol, 0.10 M in hexane),[8] at room temperature and under a nitrogen atmosphere, was added 0.15 g of methyl phenylacetate (1.0 mmol). The reaction mixture was stirred for ca. 10 min, treated with 0.12 mL of piperidine (1.2 mmol), and then monitored by TLC or GC until the reaction had gone to completion.[9] After 12 h, the reaction solution was quenched with 1 mL of methanol in order to precipitate $\mathrm{[Sn(OMe)_2]_n}$, diluted with 100 mL of ethyl acetate, and then decanted. The organic layer was washed twice with 5 mL of aqueous KF solution (5 M) and once with 10 mL

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[5] Further studies using ^{119}Sn NMR are in progress to determine the nature of the tin(II) amide in solution.

[6] A dramatic color change in the reaction solution, from orange to lemon yellow, is observed during this step.

[7] Stannylenes, of the type $\mathrm{Sn[NR_2]_2}$, R = Et, will also react with esters to give amides; however, more than 0.5 equiv of $\mathrm{Sn[NR_2]_2}$ is needed for the reaction to go to completion. This appears to be due to the fact that after the first amide substituent is transferred a $\mathrm{MeOSnNR_2}$ stannylene is generated and that stannylenes with methoxy or ethoxy substituents tend to be insoluble.

[8] Ethereal solvents can also be used. In THF the reactions are slower and with more sensitive substrates, e.g., methyl phenylacetate, minor amounts (ca. 5%) of Claisen condensation products are observed.

[9] The order of addition of the reagents is not critical.

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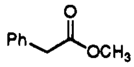
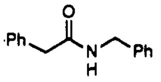
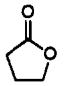
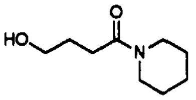
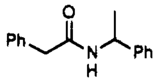
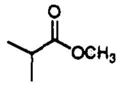
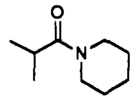
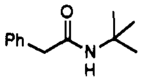
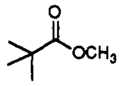
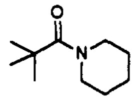
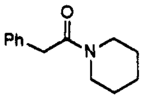
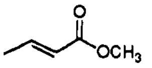
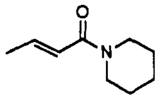
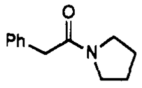
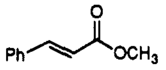
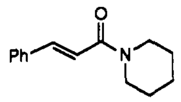
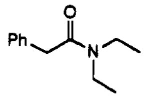
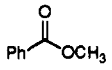
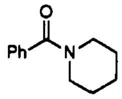
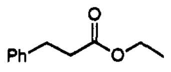
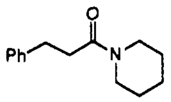
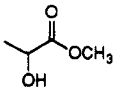
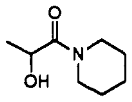
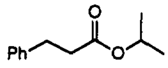
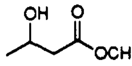
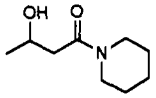
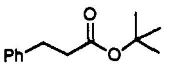
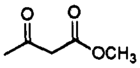
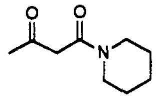
Table I. Conversion of Esters to Amides via Tin(II) Amide Reagents

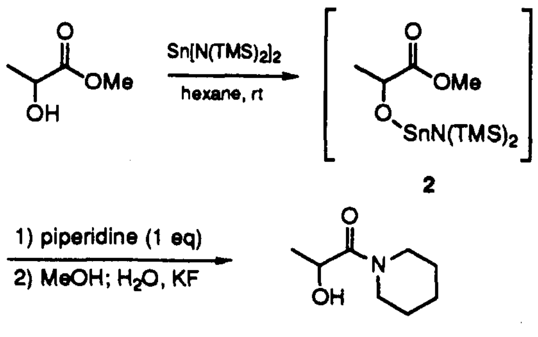
entry	ester	amide	yield	entry	ester	amide	yield
1			65	10			72
2	"		67	11			60
3	"		63	12			0
4	"		74	13			87
5	"		87	14			94
6	"		83	15			73
7			89	16			74
8		"	80	17			88
9		"	30	18			83

of brine and then dried ($MgSO_4$) and concentrated at reduced pressure. Purification of the crude product by column chromatography (8:1 hexane/ethyl acetate) gave 0.15 g (74%) of phenylacetamide piperidine as a colorless oil.

A wide range of amides can be prepared using this new methodology. For example, tin(II) amides derived from primary amines react with methyl phenylacetate to give the corresponding amides in 63–67% yield (Table I, entries 1–3). Similarly, tin(II) amides generated with secondary amines react with this ester in 74–87% yield (entries 4–6). The condensation fails, however, with tin(II) amides derived from sterically encumbered amines and aromatic amines. For example, the tin(II) amide generated from either diisopropylamine or aniline did not react with methyl phenylacetate.

After examining the condensation of a standard ester with a variety of tin(II) amides, we next evaluated the reactivity of various esters with a tin(II) amide derived from piperidine. *We were pleased to find that the reaction proceeds smoothly with all substrates that were not sterically hindered.* With a series of hydrocinnamate esters, for example, good yields were obtained with ethyl and isopropyl esters (entries 7–8). The *tert*-butyl ester, however, was converted to the amide in poor yield (entry 9).[10] With another series of esters that had increasing steric bulk at the α-carbon, only the tertiary ester did not react (entries 10–12). We also found that both aromatic and conjugated esters were readily converted to piperidinyl amides under our standard reaction conditions (entries 13–15).[11]

Our final series of experiments evaluated esters that had reactive functional groups, such as α- and β-hydroxy esters and β-keto esters. Although the mechanism of these condensations is thought to proceed via an intermediate tin(II) alkoxy amide, the overall result is the same. For example, methyl lactate was smoothly converted to a piperidinyl amide via tin(II) alkoxy amide 2 (eq 3). In the case of β-hydroxy esters as substrates, one of three dif-



(3)

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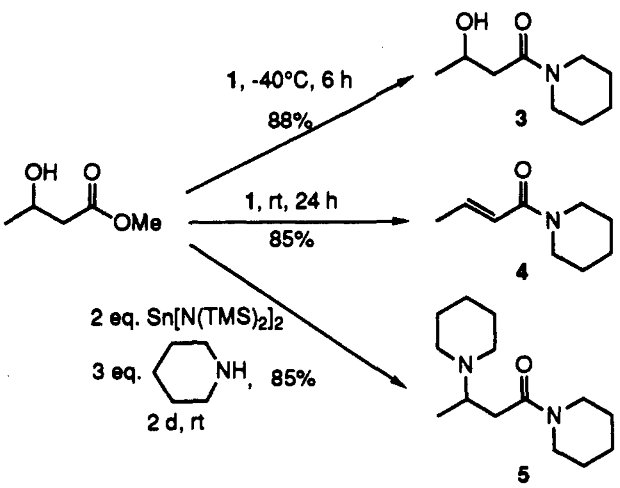
[10] There is no decomposition during this reaction, only starting material and amide are recovered.

[11] In the presence of excess tin(II) amide, conjugated esters can be converted to β-amino amides.

Scheme I



ferent products can be selectively prepared in high yield under judiciously chosen reaction conditions (Scheme I). Reaction of mixed tin(II) amide 1 with methyl 3-hydroxybutanoate at −40 °C yielded β-hydroxy amide 3, whereas reaction at room temperature gave α,β-unsaturated amide 4. Finally, reaction of the β-hydroxy ester with 2 equiv of $Sn[N(TMS)_2]_2$ and 3 equiv of piperidine for an extended period of time at room temperature produced β-amino amide 5.

Lastly, we found that β-keto esters could be converted to the corresponding β-keto amides, with no addition to the ketone being observed. Presumably, this is due to initial enolization of the ketone by $Sn[N(TMS)_2]_2$, to give a tin(II) alkoxy amide intermediate. As with α- and β-hydroxy esters, subsequent addition of an aliphatic amine is thought to form a new tin(II) alkoxy amide, followed by intramolecular transfer of the amino group.

Acknowledgment. We wish to thank the National Institutes of Health (GM42732) for support of this research.

Supplementary Material Available: General procedures and compound characterization data (6 pages). This material is contained in many 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.

Enantioselective Metal Carbene Transformations with Polyethylene-Bound Soluble Recoverable Dirhodium(II) 2-Pyrrolidone-5(*S*)-carboxylates

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Summary: Ligand displacement of methyl 2-pyrrolidone-5(*S*)-carboxylate (5(*S*)-MEPYH) from $Rh_2(5(S)\text{-MEPY})_4$ by a soluble polyethylene-bound 2-pyrrolidone-5(*S*)-carboxylate produced a recoverable dirhodium(II) catalyst whose effectiveness was demonstrated by high enantioselection for intramolecular cyclopropanation of 3-methyl-2-buten-1-yl diazoacetate (98% ee) and intramolecular C–H insertion of 2-methoxyethyl diazoacetate (72% ee) as well as by catalyst recovery and reuse seven times.

Dirhodium(II) carboxamides possessing chiral 2-pyrrolidone-5-carboxylate ligands are attractive catalysts for highly enantioselective metal carbene transformations.[1] Their applications extend from intermolecular cyclopropanation[2] and cyclopropenation[3] reactions to intramolecular cyclopropanation[4] and carbon–hydrogen insertion[5] reactions, and enantiomeric excesses greater than 90% have been realized. Constructed with four enantiomerically pure methyl 2-pyrrolidone-5-carboxylate (MEPYH) ligands so that each rhodium possesses two adjacent Rh–N bonds, $Rh_2(5(S)\text{-MEPY})_4$ and its enantiomeric form, $Rh_2(5(R)\text{-MEPY})_4$, are prepared by ligand displacement of acetate from $Rh_2(OAc)_4$ in refluxing chlorobenzene.[6] Normally used in amounts of 0.5–1.0 mol %, these catalysts are rarely recovered from experimental small-scale reactions, and there has as yet been no reliable estimate of their reuse and turnover potentials.

The recent development of anionic polyethylene carboxylates for attachment of dirhodium(II), and the successful demonstration that rhodium(II) carboxylates of terminally functionalized polyethylene carboxylic acids are effective and reusable cyclopropanation catalysts,[7] prompted our joint inquiry into the development of similarly reusable dirhodium(II) catalysts that possess chiral ligands. Consequently, polyethylene oligomers with M_n of 1500–2000 were prepared by anionic oligomerization of ethylene, carboxylated with carbon dioxide at −78 °C,[8] reduced by $Me_2S{\cdot}BH_3$ in toluene at 110 °C, and then esterified with 2-pyrrolidone-5(*S*)-carboxylic acid (eq 1). The oligomer-bound dirhodium(II) 2-pyrrolidone-5(*S*)-

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