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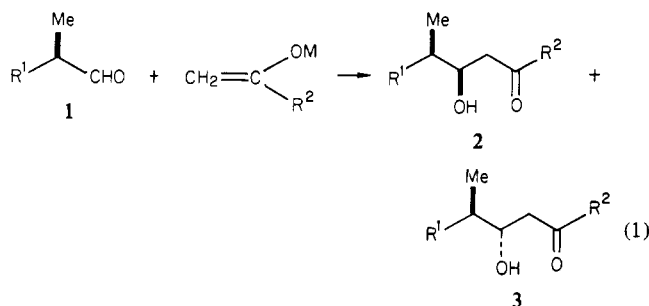
Acyclic Stereoselection. 16. High Diastereofacial Selectivity in Lewis Acid Mediated Additions of Enolsilanes to Chiral Aldehydes¹

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When a β -hydroxy carbonyl compound is formed by an aldol addition or related reaction, two distinct types of diastereoselectivity are possible. If two new stereocenters are generated in the reaction, they may have two different *relative* configurations. This kind of diastereoselectivity, termed "simple diastereoselectivity", is now well in hand as a result of an extraordinary amount of research activity during the last 5 years.² When one of the reactants is chiral, a second type of diastereoselectivity, termed "diastereofacial selectivity",³ is possible. For example, addition of a variety of lithium enolates to 2-phenylpropanal (**1a**) gives diastereomers **2a** and **3a** in ratios of about

a, R¹ = Ph; b, R¹ = PhCH₂; c, R¹ = c-C₆H₁₁; d, R¹ = Me₂C=CH

3.5:1. (eq 1, M = Li). This sort of diastereofacial preference, qualitatively predictable by Cram's rule for asymmetric induction or one of its more modern descendants,⁴ is typical for additions of complex hydrides,⁵ organometallic reagents,⁵ or lithium enolates⁶ to aldehyde **1a**. The only effective method that has been developed for dealing with the "Cram's rule problem" in additions to chiral aldehydes is double stereodifferentiation.^{3,7} Thus, by employing chiral enolate precursors, modest intrinsic diastereofacial preferences may be amplified. In favorable cases, the innate diastereofacial preference of a chiral aldehyde may even be reversed.⁸

In this communication, we report that chiral aldehydes show exceptional diastereofacial preferences in their Lewis acid mediated reactions with enolsilanes.⁹ Selected data from our study of this question are presented in Table I. With 2-phenylpropanal (**1a**),

Table I. Diastereomer Ratios in the Reactions of Lithium Enolates and Enolsilanes with Chiral Aldehydes (Eq 1)

entry	R ¹	R ²	M	conditions ^a	yield, % ^b	product ratio, 2:3
1	Ph	Me	Li	A	89	3:1
2	Ph	<i>t</i> -Bu	Li	A	80	4:1
3	Ph	MeO	Li	A	91	3:1
4	Ph	<i>t</i> -BuO	Li	A	70	4:1
5	Ph	Me ₂ N	Li	A	67	3:1
6	Ph	Me	<i>t</i> -BuMe ₂ Si	B (1.1)	75	10:1
7	Ph	<i>t</i> -Bu	<i>t</i> -BuMe ₂ Si	B (1.1)	74	24:1
8	Ph	MeO	<i>t</i> -BuMe ₂ Si	B (2.8)	81	15:1
9	Ph	<i>t</i> -BuO	<i>t</i> -BuMe ₂ Si	B (2.2)	81	36:1
10	PhCH ₂	Me	Li	A	73	1.1:1
11	PhCH ₂	MeO	Li	A	67	1.1:1
12	PhCH ₂	<i>t</i> -BuO	Li	A	65	1.1:1
13	PhCH ₂	Me	<i>t</i> -BuMe ₂ Si	B (2.5)	72	1.3:1
14	PhCH ₂	MeO	<i>t</i> -BuMe ₂ Si	B (2.6)	78	1.6:1
15	PhCH ₂	<i>t</i> -BuO	<i>t</i> -BuMe ₂ Si	B (1.8)	88	2.5:1
16	Me ₂ C=CH	<i>t</i> -BuO	Li	A	66	2:1
17	Me ₂ C=CH	<i>t</i> -BuO	<i>t</i> -BuMe ₂ Si	B (2.0)	68	25:1
18	c-C ₆ H ₁₁	<i>t</i> -BuO	Li	A	78	1.5:1
19	c-C ₆ H ₁₁	<i>t</i> -BuO	<i>t</i> -BuMe ₂ Si	B (1.5)	77	16:1

^a Method A: THF, -78 °C, 1 min. Method B: CH₂Cl₂, -78 °C, 1 equiv of BF₃·Et₂O, 1-4 h, equiv of enolsilane shown in parentheses. ^b Isolated material. The diastereomer pairs were not separated.

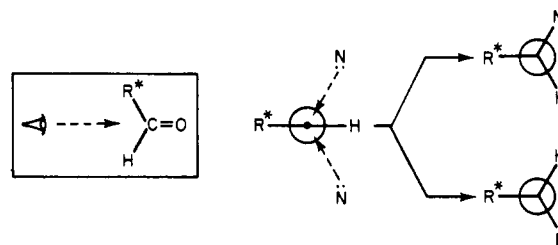
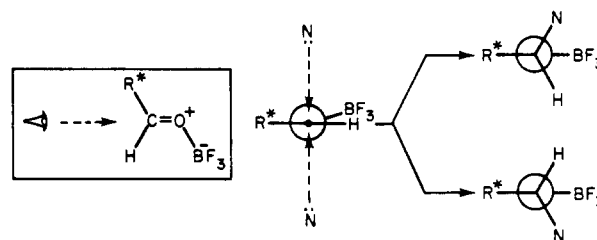


Figure 1. Reaction of a nucleophile with an aldehyde.

Figure 2. Reaction of a nucleophile with a BF₃-coordinated aldehyde.

the diastereofacial preference is significantly higher with all four enolsilanes studied than with the corresponding lithium enolates. The most selective reagent, from a preparative standpoint, is the *tert*-butyldimethylenolsilane derived from *tert*-butyl acetate; the reaction of this material with aldehyde **1a** gives as product the β -hydroxy ester of 97.3% diastereomeric purity. Similar results are seen with chiral aldehydes **1c** and **1d**. Even aldehyde **1b**, which shows essentially no diastereofacial preference with lithium enolates (entries 10-12), exhibits a modest preference with the *tert*-butyldimethylenolsilane derived from *tert*-butyl acetate (entry 15).

The reason for this striking difference in stereoselectivity has not yet been fully elucidated. It may be due to the fact that, in the normal addition of a nucleophile to an aldehyde, a trajectory is followed that brings the nucleophile closer to H than to R (Figure 1). Thus, asymmetry in R is transferred imperfectly to the newly created chiral center. Any structural change that serves to bring this approach trajectory back toward the perpendicular would increase the interaction between N and R*, and thus increase the effective asymmetric induction of the process. This hypothesis is consistent with the observation that asymmetric induction increases markedly in the series of compounds **4** as the

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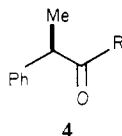
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size of R increases.¹⁰ When a Lewis acid coordinates with an aldehyde, it probably occupies the position syn to the hydrogen. Thus, a nucleophile may be forced to approach the carbonyl plane in a more perpendicular fashion, resulting in greater stereoselection (Figure 2).

It should be noted that Danishefsky and co-workers have also observed high diastereofacial preferences in Lewis acid mediated cycloadditions of silyloxydienes to chiral aldehydes, including aldehyde 1a.¹¹ Evidence has recently been developed that, at least under some conditions, the latter process proceeds by a two-step mechanism involving an initial aldol-type addition of the enolsilane to the Lewis acid coordinated aldehyde. An explanation similar to that presented in Figures 1 and 2 has also been advanced by Danishefsky.¹¹ Further experiments aimed at elucidating the nature of the transition state in the Mukaiyama aldol reaction are in progress.

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Supplementary Material Available: Experimental methods and analytical data for the compounds used (11 pages). Ordering information is given on any current masthead page.

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Convenient Direct Synthesis of (SN)_x Films from S₄N₄ at Lower Temperatures

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The outstanding conducting properties of both (SN)_x and halogenated (SN)_x have been of widespread interest in recent years.¹ All previously reported syntheses of (SN)_x require complicated chemical reactions² or the dangerous³ pyrolysis of S₄N₄¹ or substitutes⁴ over silver or quartz wool at 200 °C to form S₂N₂, which topochemically polymerizes at room temperature.

We report here a synthesis of (SN)_x that excludes all these disadvantages.⁵ Earlier work has shown⁶ that a radio frequency glow discharge is a convenient source for the generation of radicals by homolytic cleavage of small molecules in the gas phase, which

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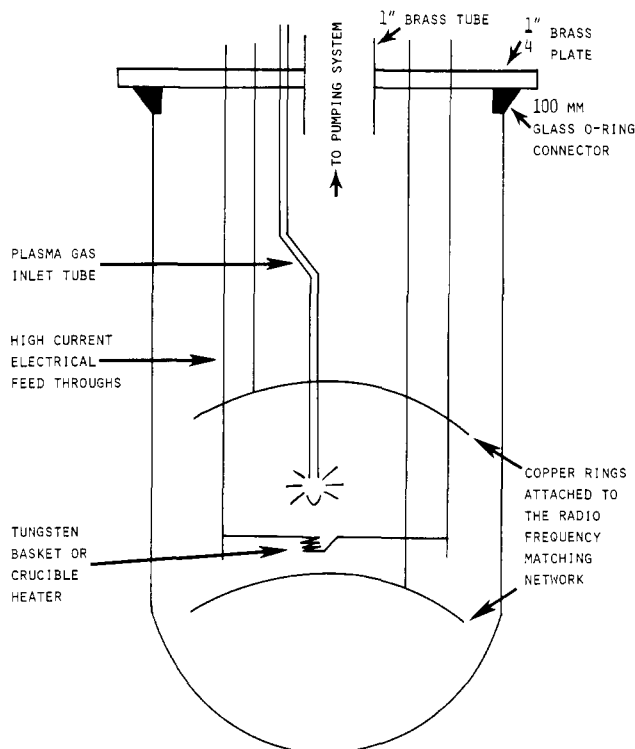
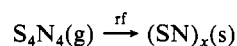


Figure 1.

were reacted with metal atoms to form a wide variety of σ -bonded compounds.

In a similar manner, S₄N₄ can be sublimed at 70–80 °C into a helium plasma by using the reactor shown in Figure 1. The S₄N₄ is placed in a quartz crucible and is heated resistively by using a tungsten crucible heater. The helium is slowly metered into the reactor through the plasma gas inlet tube. By attaching the two power leads from a Tegal Corp. 100-W radio frequency power supply to two internal copper rings, the radio frequency power can be capacitively coupled to the plasma gas. The Pyrex reactor vessel is submerged in liquid nitrogen, which rapidly condenses the products as they are formed.

A 10-MHz radio frequency discharge at a power level of 40 W yields a greenish-blue film with metallic lustre on the reactor walls:



This material contains a mixture of (SN)_x and unreacted S₄N₄. The latter was separated by washing with CH₂Cl₂ to yield pure (SN)_x. Thus, 0.5 g of S₄N₄ can be converted in a 3-h period to yield ca. 0.25 g of (SN)_x, which was identified⁷ by chemical properties, IR spectra,⁸ elemental analysis,⁹ and powder pattern X-ray data.¹⁰ A minor amount of volatile products condensed in a trap were identified as S₄N₂¹¹ and oligomers of SN, which slowly converted into (SN)_x.¹²

Our initial attempts at direct fluorination of (SN)_x to yield a fluorinated polymer were unsuccessful. Instead, the products were identical with those obtained by direct fluorination of S₄N₄.¹³ Since the halogenated (SN)₂ contains Br₃⁻ and ICl₂⁻ units be-

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(9) Anal. Calcd: N, 30.4. Found: N, 27.3.

(10) Cu K α radiation, unfiltered, 2 θ , I (estimated intensity) 23.7, 1; 26.4, 8; 29.9, 3; 32.8, 9; 35.4, 9; 40.7, 10; 43.8, 2; 47.0, 10; 52.9, 10; 56.0, 3; 66.0, 2; 68.2, (1); 72.7, (1); 77.2, 1; 85.7, 1; 94.5, (1).

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