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RHODIUM(II) (*S*)-*N*-(ARYLSULFONYL)PROLINATE CATALYZED ASYMMETRIC INSERTIONS OF VINYL- AND PHENYLCARBENOIDS INTO THE Si-H BOND

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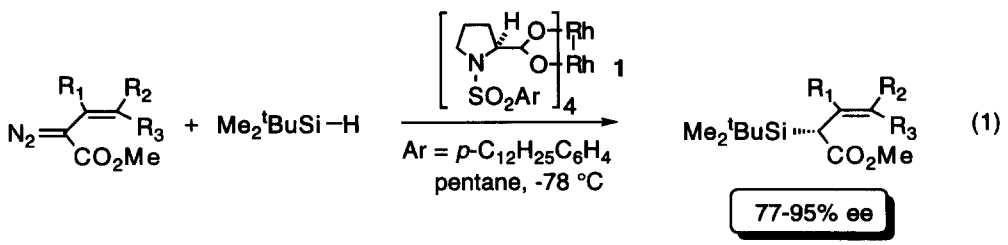
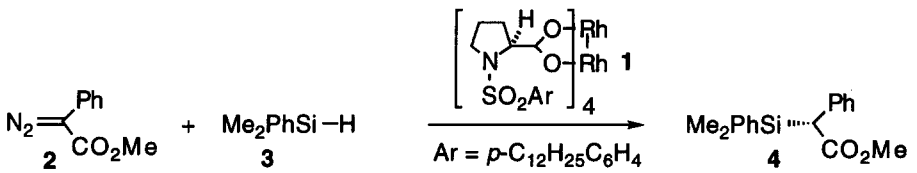
Abstract: Allylsilanes or benzylsilanes of high enantiomeric purity (77-95% ee) are formed from the rhodium(II) (S)-N-[p-(dodecylphenyl)sulfonyl]prolinate (1) catalyzed decomposition of vinyldiazomethanes or phenyldiazomethanes in the presence of dimethylphenylsilane (3).

Allylsilanes are versatile intermediates in organic synthesis since they can be used in a variety of stereoselective transformations.[1] An attractive approach for the formation of allylsilanes is the Si-H insertion of vinylcarbenoids into trialkylsilanes.[2] Landais and co-workers have reported that racemic allylsilanes of defined alkene geometries may be readily formed through rhodium(II) acetate catalyzed decomposition of vinyldiazomethanes in the presence of trialkylsilanes.[3] Furthermore, by using (*R*)-pantolactone as a chiral auxiliary on the vinyldiazomethane, it was possible to produce the allylsilanes in 32-70% de.[3] Recently, an alternative approach for asymmetric insertion into the Si-H bond was described using a series of chiral rhodium(II) carboxylates and carboxamides.[4] Using phenyldiazomethane as substrate, Si-H insertions were achieved in 7-47% ee.[4] Absent from the catalysts surveyed were rhodium(II) (*S*)-*N*-(*p*-alkylphenyl)sulfonylprolinates which have been shown to be excellent catalysts for asymmetric cyclopropanations by vinylcarbenoids[5] and phenylcarbenoids[6] (up to 98% ee). In this paper, we describe that rhodium(II) (*S*)-*N*-[*p*-(dodecylphenyl)sulfonyl]prolinate (**1**)[5c] is a very effective catalyst for asymmetric Si-H insertion reactions, leading to benzylsilanes and allylsilanes in 77-95% ee (eq 1).



(1)

The utility of the rhodium prolinate catalyst **1** for asymmetric Si-H insertions was initially determined using the standard reaction conditions that were recently reported by Doyle and Moody.[4] Rhodium(II) prolinate **1** catalyzed decomposition of methyl phenyldiazoacetate (**2**) in the presence of dimethylphenylsilane (**3**) in dichloromethane at room temperature resulted in the formation of the insertion product **4**[4] in a very disappointing 3% ee. It is well established, however, that phenylcarbenoid and vinylcarbenoid cyclopropanations catalyzed by rhodium prolinates proceed in much higher levels of asymmetric induction when hydrocarbon solvents are used instead of dichloromethane. A similarly dramatic effect was seen in these asymmetric Si-H insertion reactions. Repeating the reaction for the decomposition of **2** by the rhodium catalyst **1** using pentane as solvent at room temperature resulted in the formation of **4** in 36% ee. Further improvement in enantioselectivity was possible by conducting the reaction at lower temperatures; at -78 °C, **4** was formed in 85% ee. The absolute stereochemistry of **4** was determined to be *R* by conversion of **4** to (*R*)-(+)-1-phenyl-1,2-ethanediol by the procedure developed by Landais.[3]

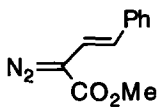
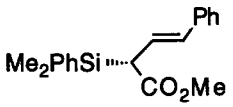
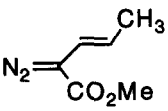
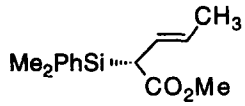
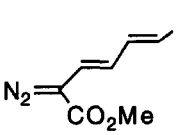
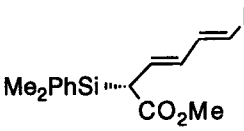
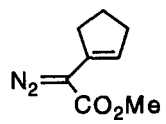
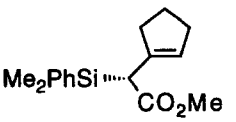
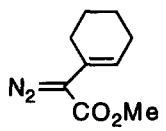
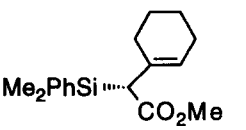


entry	temp	solvent	yield, %[a]	ee , %[b] (abs. config.)
1	25	CH_2Cl_2	63	-3 (*S*)
2	25	pentane	65	36 (*R*)
3	0	pentane	52	51 (*R*)
4	-78	pentane	50	85 (*R*)

a: Isolated yield after distillation. b: Enantiomeric excesses (ee's) determined by HPLC (Chiracel OD column, 5% 2-propanol : 95% hexane)

The catalytic asymmetric Si-H insertion can be extended to prepare a series of allylsilanes as shown in Table 1. Rhodium(II) prolinate **1** catalyzed decomposition of the vinyldiazomethanes **5** at -78 °C resulted in the formation of the allylsilanes **6** in 77-95% ee. The enantiomeric purity of the allylsilanes **6** was readily determined by the use of chiral shift reagents. The absolute stereochemistry of **6a** was determined to be *R* by conversion of **6a** to (*R*)-(+)-4-phenyl-1,2-butanediol by the standard procedure developed by Landais.[3] Therefore, it appears that **1** results in the opposite asymmetric induction to that observed when (*R*)-pantolactone was used as a chiral auxiliary, a trend that was also seen in the asymmetric cyclopropanations.[5c,7] The yields of **6** were determined by NMR integration using 1,4-dimethoxybenzene as an internal standard, since **6** underwent partial decomposition on attempted purification by distillation or chromatography. Even though these allylsilanes may not be readily purified, it has already been shown that the racemic allylsilanes can be effectively used in further stereoselective transformations.[2a,3] The enantioselectivity in these Si-H insertions is much higher than the values obtained using (*R*)-pantolactone as a stoichiometric chiral auxiliary on the vinylcarbenoid,[3] the alternative method for asymmetric vinylcarbenoid transformations.[7]

Table 1. Rhodium(II) prolinate **1** catalyzed decomposition of vinyldiazomethanes **5** in the presence of **3**.

substrate	product	yield, %[a]	ee, %[b] (abs. config.)
 **5a**	 **6a**[3]	76	91 (*R*)[c]
 **5b**	 **6b**	64	95 (*R*)[d]
 **5c**	 **6c**[3]	68	77 (*R*)[d]
 **5d**	 **6d**	63	85 (*R*)[d]
 **5e**	 **6e**	77	92 (*R*)[d]

a: Yield determined using 1,4-dimethoxybenzene as an internal standard. b: Enantiomeric excesses (ee's) determined by ^{1}H NMR using praseodymium(III) tris[3-(heptafluoropropylhydroxymethylene)-(-)-camphorate] as a chiral shift reagent. c: Assigned by conversion of **6a** to (*R*)-(+)-4-phenyl-1,2-butanediol.[3] d: Tentatively assigned on the assumption that the asymmetric induction parallels that for the formation of **4** and **6a**.

In summary, the rhodium(II) prolinate complex **1** was shown to be an excellent catalyst for the asymmetric synthesis of benzyl- and allylsilanes. These studies demonstrated once again the remarkable effect that a non-polar solvent has on the extent of asymmetric induction when using **1** as the catalyst. Furthermore, the high solubility of **1** in hydrocarbon solvents enables the Si-H insertions to be carried out at low temperatures, which results in further improvement of the asymmetric induction. Some of the racemic allylsilanes have already been exploited for further stereoselective transformations,[3] and the availability of these compounds in enantioenriched form will greatly expand their synthetic utility.[8]

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