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Rhodium(II)-Vinylcarbenoid Insertion into the Si-H Bond. A New Stereospecific Synthesis of Allylsilanes.

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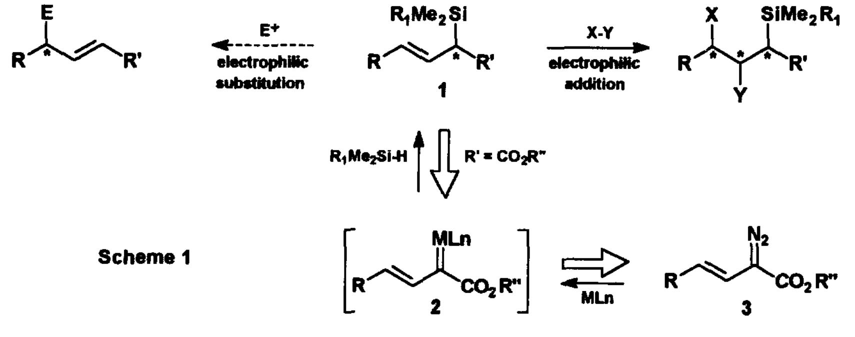
Abstract: $Rh_2(OAc)_4$ catalysed decomposition of vinyldiazocarbonyl compounds in the presence of organosilanes led *stereospecifically* to the corresponding allylsilanes in good yields. An asymmetric approach has also been considered as well as the extension of the methodology to the synthesis of other allylic systems.

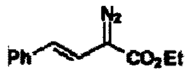
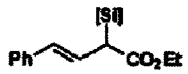
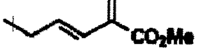
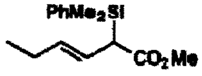
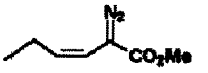
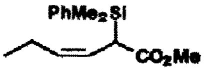
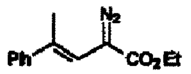
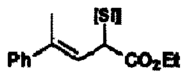
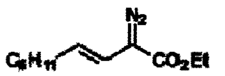
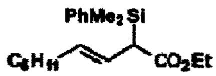
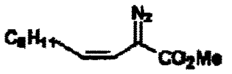
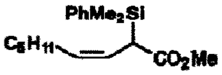
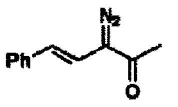
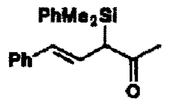
The stereocontrolled functionalization of the double bond of chiral allylsilanes (*i.e.* **1**) has recently attracted considerable interest (Scheme 1).[1] The high stereoselectivities arising from such functionalization actually allow for the construction of a variety of complex acyclic synthons. However, such a strategy requires that the configuration of both the chiral centre and the double bond of the starting allylsilane are perfectly set up.[2] This often is a tedious problem to solve. Recent studies from this laboratory[3a-b] and others[3c-d] have shown that rhodium-carbene insertion into the Si-H bond is an efficient process for the formation of the C-Si bond. Extension of this methodology to vinylcarbenoid species (*i.e.* **2**), available from vinyldiazoesters **3**, would provide an easy entry to allylsilanes possessing a useful ester function on the allylic chiral centre. This approach should prevent any modification of the double bond geometry, since the insertion process is expected to take place regiospecifically α to the ester group. We report herein our preliminary results on the stereocontrolled synthesis of allylsilanes such as **1** ($R'=CO_2R''$), and on the development of an asymmetric approach which has also been extended to other allylic analogs.



Scheme 1

The vinyldiazocarbonyl compounds **3a-h** were prepared using the procedure of Davies,[4] starting from the corresponding β,γ-(*E*) and (*Z*)-unsaturated esters or ketone.[5] As summarised in Table 1, diazoesters **3a-f** all underwent smooth insertion reactions, whatever the nature of the silane, giving rise in good yields to allylsilanes **1a-f**, pure enough to be used without further purifications.[6] Most interesting is the observation that *the geometry of the double bond is totally retained during the insertion process*, thus giving access *stereospecifically* to (*Z*) or (*E*) allylsilanes. This gives our method considerable potential, since the double bond geometry is easily set up during the preparation of **3a-f**. The methodology has also been applied to dienyldiazoester **3g** and vinyldiazoketone **3h**, both giving the desired insertion products **1g** and **1h** in reasonable yields.

Table 1. Synthesis of allylsilanes using rhodium-vinylcarbenoid insertion into the Si-H bond (Scheme 1).

Entry	Substrate[a,b]	Product[b,c]	Yield (%)[d]
1	 **3a**	 **1aa**, [Si] = $PhMe_2Si$ **1ab**, [Si] = (5-Me-thienyl)Me_2Si **1ac**, [Si] = $(TMS)_3Si$	70 72 45
2	 **3b**	 **1b**	73
3	 **3c** (*Z/E* ratio 96:4)	 **1c** (*Z/E* ratio 95:5)	75
4	 **3d**	 **1da**, [Si] = $PhMe_2Si$ **1db**, [Si] = (5-Me-thienyl)Me_2Si	80 61
5	 **3e**	 **1e**	76
6	 **3f** (*Z/E* ratio >98:2)	 **1f** (*Z/E* ratio >98:2)	72
7	 **3g**	 **1g**	72
8	 **3h**	 **1h**	65

[a] Prepared from the corresponding ester or ketone: *p*-acetamidobenzenesulfonyl azide (1.2 eq.), DBU (1 eq.) in CH_3CN, 0°C, 1-4 h.[4] [b] *E/Z* ratio >98:2 unless indicated (^1H NMR). [c] Standard conditions : the diazoester (1 eq.) in CH_2Cl_2 was added slowly at RT (syringe pump, 1 µmol/min), to a mixture of silane (2 eq.) and $Rh_2(OAc)_4$ (1 mol%) in CH_2Cl_2, except for **3g** which was mixed with $PhMe_2SiH$ (5 eq.) prior to addition of the rhodium catalyst. [d] Yields obtained after removal under vacuum of the solvent and the excess of silane. Distillation of these esters gave pure compounds in somewhat lower yields due to decomposition.[6]

Having designed an efficient entry to racemic allylsilanes such as **1a-h**, we then examined the asymmetric version of the methodology. We previously showed that by using menthyl or camphor α-substituted-α-diazoesters, the corresponding α-silylacetic esters could be obtained in good yields, but, with somewhat modest diastereoselectivities.[3b] We thus turned our attention to (*R*)-pantolactone, a chiral auxiliary which has been shown to be very efficient in asymmetric cyclopropanations with vinylcarbenoids.[7] As demonstrated by Davies, this efficiency might arise from co-ordination of the carbon of the C=Rh bond to the pantolactone carbonyl (Fig.-1), which leads to a rigidification of the transition state, and hence to improved selectivities compared to non co-ordinating chiral auxiliaries (*e.g.* menthol).[8] In order to test the validity of this assumption in our insertion, we prepared vinyldiazoesters **4a-c** as described above,[7,9] and submitted them to the insertion reaction. The results summarised in Table 2 show that reasonable levels of diastereoselectivity are attained (entry 2 and 3), but yet not as high as those reported in cyclopropanations. However some observations suggest that as in cyclopropanation, the co-ordination described above might be operating here. For example, the small difference in steric hindrance between substrates **4a** and **4b** (entry 1 and 2) cannot explain the difference in diastereoselectivities observed in these cases. We assume that the more electron-rich vinyldiazoester **4a** probably leads to a weaker co-ordination, due to the lower electrophilicity of the carbon of the C=Rh bond. The better diastereoselectivity observed with the (*Z*)-isomer **4c** compared to the (*E*)-isomer **4b** (entry 2 and 3) is more intriguing and has not been rationalized so far. Lastly, an attempt to increase the diastereoselectivity by using a sterically hindered silane such as $(TMS)_3SiH$ led to a lower yield (entry 4) and the same selectivity as that obtained with $PhMe_2SiH$ (entry 1). This might reflect the fact that hydrogen, and not silicon, is transferred first onto the asymmetric metal-carbene after oxidative addition.[3b]

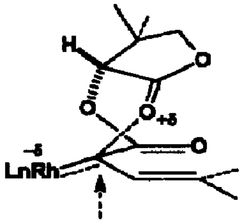
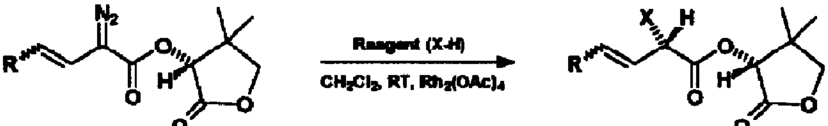


Fig.-1

Finally, we carried out comparative studies between rhodium-vinylcarbenoid insertion into Si-H and O-H bonds. Surprisingly, and contrary to recent observations made by Moody,[10] insertion into the O-H bond of MeOH led to almost no selectivity (entry 6). Conversely, insertion into the O-H bond of H_2O (entry 5) gave a higher diastereoselectivity than that obtained with the Si-H bond and led to a product of identical absolute configuration (S)[11] (entry 1 and 5). This stereochemical outcome could be explained by a nucleophilic attack of H_2O on the electrophilic metal-carbene, through a transition state close to the one reported by Davies[7] for cyclopropanation (Fig.-1). Our mechanistic studies about the insertion of metal-carbenoid into the Si-H bond are not yet conclusive (*i.e.* oxidative addition of the Si-H bond followed by Si or H migration[3b]) and do not allow us to draw a definitive picture concerning the transition state of the insertion into the Si-H bond.



Scheme 2

Table 2. Asymmetric insertion of rhodium-vinylcarbenoids into X-H bonds (Scheme 2).

Entry	R	Double bond geometry	Substrate	Reagent (X-H)[a]	Product (X)	Yield (%)	d.e. (%)[b]	Config.[c]
1	Ph	E	**4a**	$PhMe_2SiH$	**5a**, ($PhMe_2Si$)	67	32	S
2	Et	E	**4b**	$PhMe_2SiH$	**5b**, ($PhMe_2Si$)	67	50	S
3	Et	Z	**4c**	$PhMe_2SiH$	**5c**, ($PhMe_2Si$)	75	70	S
4	Ph	E	**4a**	$(TMS)_3SiH$	**5d**, ($(TMS)_3Si$)	55	34	n.d.[d]
5	Ph	E	**4a**	H_2O[e]	**5e**, (OH)	75	50	S
6	Ph	E	**4a**	MeOH[f]	**5f**, (OMe)	75	5	n.d.[d]

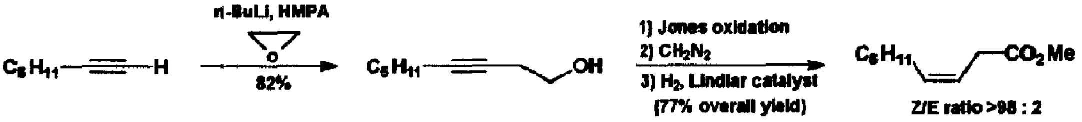
[a] 2eq. [b] Determined from ^1H NMR of the crude esters. [c] Absolute configuration of the major isomer was determined as described in reference 11. [d] Not determined. [e] Moist ether was used as solvent instead of CH_2Cl_2. [f] MeOH was used as solvent.

Further studies are now under way in order to gain more insight into the effects governing the stereoselectivity of these insertions. These studies and the further functionalizations of our allylsilanes will be reported in due course.

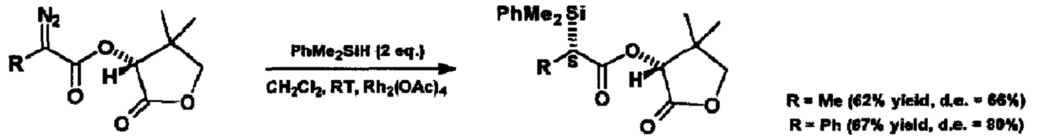
Acknowledgements. The authors gratefully acknowledge the *Swiss National Science Foundation* for generous support, Pr. P. Vogel and Dr. I.M. Eggleston for fruitful discussions. We thank Dr. R. Cloux for NMR facilities.

References and Notes

1. (a) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.*, **1989**, *37*, 57-575; (b) Murphy, P.J.; Russell, A.T.; Procter, G. *Tetrahedron Lett.*, **1990**, *31*, 1055-1058; (c) Murphy, P.J.; Procter, G. *ibid.*, **1990**, *31*, 1059-1062; (d) Ward, R.A.; Procter, G. *ibid.*, **1992**, *33*, 3363-3366; (e) Fleming, I. *J. Chem. Soc. Perkin Trans 1*, **1992**, 3363-3369; (f) Bassindale, A.R.; Taylor, P.G.; Xu, Y. *ibid.*, **1994**, 1061-1067; (g) Sparks, M.A.; Panek, J.S. *J. Org. Chem.*, **1991**, *56*, 3431-3438; (h) Coppi, L.; Mordini, A.; Taddei, M. *Tetrahedron Lett.*, **1987**, *28*, 969-972.
2. (a) Sarkar, T.K. *Synthesis*, **1990**, 969-983 and 1101-1111; (b) Bhushan, V.; Lohray, B.B.; Enders, D. *Tetrahedron Lett.*, **1993**, *34*, 5067-5070 and references cited therein.
3. (a) Andrey, O.; Landais, Y.; Planchenault, D. *Tetrahedron Lett.*, **1993**, *34*, 2927-2930; (b) Landais, Y.; Planchenault, D. *ibid.*, **1994**, *35*, 4565-4568; (c) Bagheri, V.; Doyle, M.P.; Taunton, J.; Claxton, L.E. *J. Org. Chem.*, **1988**, *53*, 6158-6160; (d) Mak, C.C.; Tse, M.K.; Chan, K.S. *ibid.*, **1994**, *59*, 3585-3589.
4. Davies, H.M.L.; Clark, T.J.; Smith, H.D. *J. Org. Chem.*, **1991**, *56*, 3817-3824 and references cited therein.
5. The precursor of **3c** was prepared in 2 steps from commercially available (*Z*)-hex-3-enol (*Z/E* 96:4) : Jones oxidation followed by esterification (CH_2N_2). Similarly, diazoester **3f** was prepared from the corresponding ester, obtained by the following sequence :



6. Analytical samples obtained by distillation gave satisfactory elemental analysis.
7. Davies, H.M.L.; Huby, N.J.S.; Cantrell, W.R., Jr.; Olive, J.L. *J. Am. Chem. Soc.*, 1993, *115*, 9468-9479 and references cited therein.
8. Higher diastereoselectivities were indeed obtained with non-allylic systems, using pantolactone instead of menthol (R = Me, 44% d.e.) :



9. During esterification using the suitable (*Z*)-acid chloride and pantolactone in the presence of NEt_3, isomerization of the (*Z*) double bond sometimes occured. Esterification is then best carried out as follows : acid (1 eq.), pantolactone (1.05 eq.), 1,3-dicyclohexylcarbodiimide (1.1eq.), DMAP (cat.) in CH_2Cl_2, RT, 2h, (75-85% yield).
10. 44% d.e. has been obtained during insertion into the O-H bond of MeOH, using 8-phenylmenthyl phenyldiazoacetate, see : Aller, E.; Cox, G.G.; Miller, D.J.; Moody, C.J., *Tetrahedron Lett.*, **1994**, *35*, 5949-5952.
11. The absolute configuration of the resulting α-silylacetic esters **5a-c** has been determined through their conversion into known homochiral 1,2-diols[3b] using the following sequence : [(i) H_2/Pd-C 10%, iPrOH; (ii) DIBAH (2 eq.); (iii) $Hg(OAc)_2$, CH_3CO_3H], then comparison of their rotations with the literature, respectively : **5a**: Jeong, K.-S.; Sjö, P.; Sharpless, K.B. *Tetrahedron Lett.*, **1992**, *33*, 3833-3836; **5b** and **5c** : Regeling, H.; Chittenden, G.J.F. *Carbohydr. Res.*, **1991**, *216*, 79-91. Absolute configuration of **5e** was determined as follows : [(i) H_2/Pd-C 10%, MeOH; (ii) LiOOH; (iii) CH_2N_2] to give the corresponding methyl-2-hydroxy-4-phenylbutanoate : Corey, E.J.; Link, J.O. *Tetrahedron Lett.*, **1992**, *33*, 3431-3434. Both sequences gave some epimerization (20-30%), but allowed us to assign unambiguously the (S) configuration for **5a-c** and **5e**.

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