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A Stereochemical Study on the Intramolecular Hydrosilylation of α,β-Unsaturated Esters

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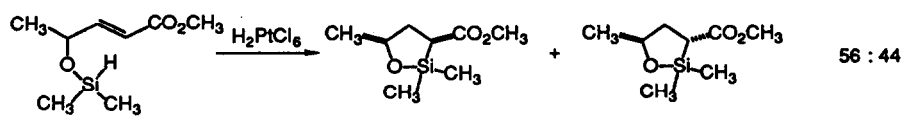
Key Words: Platinum-catalyzed, intramolecular hydrosilylation; diastereoselectivity; $A^{1,2}$ strain

***Abstract:** The intramolecular hydrosilylation of several 3-methyl-4-siloxy-2-butenoates afforded cis disubstituted lactones after desilylation. The diastereoinduction was sensitive to the bulk of the allylic substituent, but not to the groups on silicon. The origin of asymmetric induction is believed to be the $A^{1,2}$ strain from the β-methyl group.*

The hydrosilylation reaction is a widely used method for the sila-functionalization of unsaturated compounds containing carbonyl, olefinic, and acetylenic moieties.[1] The platinum or rhodium catalyzed processes have been extensively studied.[2] An important variant of this reaction is the intramolecular hydrosilylation of allylic and homoallylic alcohols reported by Tamao.[3] These reactions produce siloxacycles that are transformed into 1,3-diols by oxidative cleavage of the carbon-silicon bond. By taking advantage of the preference for five-membered ring formation a modest 1,n-induction for both allylic and homoallylic alcohols was established. Bosnich has recently reported the first systematic study of asymmetric catalysis of intramolecular hydrosilylation of allylic alcohols using chiral phosphine modified rhodium catalysts.[4] Our interests focused on the intramolecular hydrosilylation of α,β-unsaturated esters with the following objectives in mind: 1) electronically control the regioselectivity, 2) improve the yield and rate of reaction with trisubstituted olefins, 3) suppress the isomerization of the olefin, 4) examine the extent of 1,2-induction with various allylic substituents and 5) examine the role of the silyl ligands in relative asymmetric induction.

Preliminary experiments[5] with the dimethylsilyl ether of methyl (*E*)-4-hydroxypentenoate using Speier's catalyst illustrated the importance of β-substitution, Scheme 1. Thus, while the reaction was rapid, clean and regioselective, the asymmetric induction was poor. To examine the effect of allylic substituents on the diastereoselectivity of the intramolecular hydrosilylation reaction we surveyed a series of substituted 3-methyl-4-siloxy-2-butenoates, **3**.

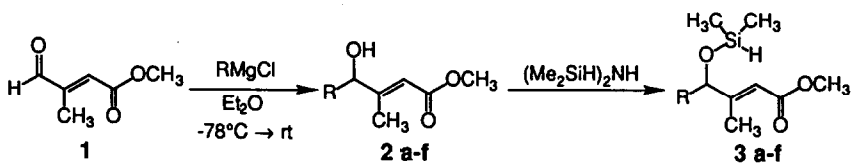
Scheme 1



The synthesis of the β,γ-disubstituted butenoates (Scheme 2) was achieved through the common intermediate **1**.[6] The requisite silyl ethers were prepared in straightforward manner by Grignard addition to **1**

followed by treatment of the resulting allylic alcohol **2** with excess 1,1,3,3-tetramethyldisilazane.[3b] Since the silyl ethers are extremely labile they must be used immediately after distillation to avoid desilylation.

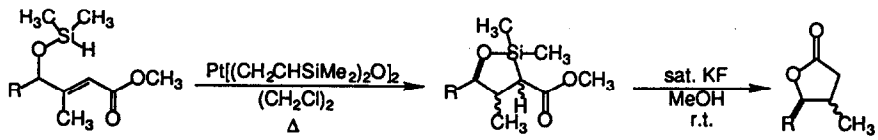
Scheme 2



a, R = Me; **b**, R = Et; **c**, R = *i*-Bu; **d**, R = Ph; **e**, R = *i*-Pr; **f**, R = *t*-Bu

Each of the 3-methyl-4-siloxy-2-butenoates was subjected to platinum-catalyzed (2 mol %) intramolecular hydrosilylation in 1,2-dichloroethane (rt to 55°C / 1 h; 55°C to 60°C / 3h). Using Speier's catalyst, desilylation of the starting silyl ether was competitive with cyclization. Thus, a neutral Pt(0) catalyst $Pt[[(CH_2CH)Me_2Si]_2O]_2$[3b,7] was employed and was found to catalyze the cyclization of each silyl ether as efficiently as Speier's catalyst without competitive desilylation. (Several rhodium complexes were surveyed as well but no cyclization was observed). After completion of the reaction, the catalyst was removed by stirring the mixture with EDTA•2Na in hexane overnight followed by filtration. Protiodesilylation was accomplished by treatment the siloxycyclopentane with saturated potassium fluoride[8] in methanol at rt for ten hours. Spontaneous lactonization of each γ-hydroxy ester was observed. In each example no erosion in selectivity was detected during this transformation. The results of this study are collected in Table 1.

Table 1. Intramolecular Platinum-Catalyzed Hydrosilylation of **3a-f**.[a]



entry	substrate	R	selectivity, 4[b]	selectivity, 5[c] cis / trans	yield, %[d]	ratio 5 / 2
1	**3 a**	Me	76:24	77:23	87	85:15
2	**3 b**	Et	77:23	78:22	73	82:18
3	**3 c**	*i*-Bu	83:71	81:19	83	82:18
4	**3 d**	Ph	92:8[d]	91:9	69	67:33
5	**3 e**	*i*-Pr	94:6	93:7	37	38:62
6	**3 f**	*t*-Bu	98:2	98:2	21	34:66

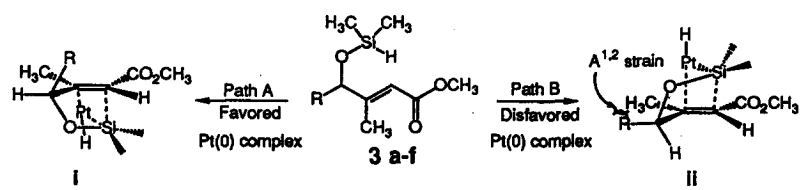
[a] Reaction Conditions: (1) $Pt[(Me_2vinylSi)_2O]_2$ (ca. 2 mol %) / $ClCH_2CH_2Cl$ / rt → 55°C / 1 h; 55°C / 3 h, (2) sat. KF / MeOH / rt / 10 h. [b] Determined by GC analysis. [c] Determined by ^1H NMR analysis. [d] Overall yield based on two synthetic transformations.

The data in Table 1 clearly indicate that both the overall yields and the stereoselectivities were highly dependent on the size of the R group. For two synthetic transformations the yields of **5** ranged from 87% for methyl to 21% for *t*-butyl. Due to their instability the siloxycyclopentane intermediates **4** were directly treated

with potassium fluoride without purification. After desilylation, only the γ-lactone **5** and the starting allylic alcohol **2** were observed. (Control experiments established that reversion of the siloxycyclopentane to the initial allylic alcohol was *not* a viable pathway). The data also indicate a direct relationship between the size of the substituent at the C-4 position and the stereochemical outcome of these reactions. In all cases the cis isomer predominated,[9] but the selectivity ranged from 77:23 for R = methyl to 98:2 for R = *t*-butyl. Branching at the C-5 position has a more pronounced effect than branching at C-6 (entry 3, Table 1).

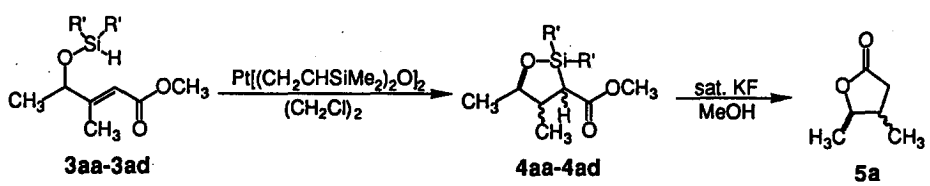
The observed selectivities are adequately rationalized by considering the transition state models for the intramolecular hydrosilylations proposed by Bosnich.[4c] These models are based on the assumption that the Pt-and Rh-catalyzed hydrosilylations proceed by the same mechanism, i.e., silyl olefin insertion is the stereochemistry determining step. Examination of these models indicates that both a *net* syn addition[4c] of the Si-Pt unit is occurring and that this reaction is governed by allylic-1,2 strain, Scheme 3. The preferred reaction Path A can accommodate the structural requirements of the presumed reactive intermediate with minimal allylic strain. On the other hand, in reaction via Path B, the intermediate **ii** experiences increasingly greater allylic strain as the size of R increases.

Scheme 3



We next examined the effect of substituents on silicon to facilitate the isolation and purification of **4** and to influence the stereoselectivity of the reaction. For this study the substrate showing the lowest selectivity was chosen, **3a**. As expected, the intermediates could be isolated and purified, but the improvement in diastereoselectivity was negligible, Table 2. Moreover, for **3ab**-**3ac** the ratio of **5** / **2** was very unfavorable. Control experiments indicated that the reappearance of **2** was due to formation of a by-product which could not proceed to siloxycyclopentane. The use of larger silyl groups in substrates derived from **2b** or **2c** lead to the exclusive recovery of the alcohol via the non-productive pathway.

Table 2. Silicon Substituent Effect in the Intramolecular Hydrosilylation.[a]

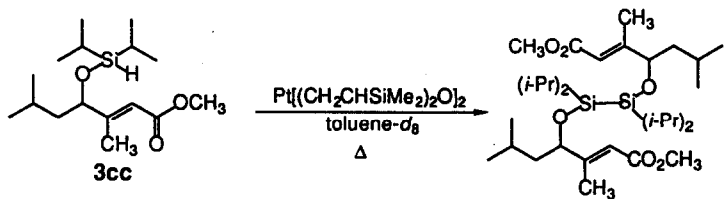


entry	substrate	R'	selectivity, 4aa-4ad[b]	selectivity, 5a[b,c]	ratio, 5 / 2
1	3aa	Me	76:24	77:23	85:15
2	3ab	-$(CH_2)_5$- [10a]	61:39	62:38	69:31
3	3ac	*i*-Pr[10b]	81:19	80:20	55:45
4	3ad	*t*-Bu	-	-	-

[a] Reaction Conditions: (1) Pt[(Me2vinylSi)2O]2 (ca. 2 mol %) / $ClCH_2CH_2Cl$ / rt → 55°C / 1 h; 55°C / 3 h, (2) sat. KF / MeOH / rt / 10 h. [b] Determined by GC analysis. [c] Determined by ^1H NMR analysis.

We suspect that the unproductive pathway involves an oxidative dimerization to a disilane as shown in Scheme 4. This process has been proposed in the literature[4] and is a reasonable alternative for sluggish hydrosilylations. Treatment with KF should regenerate 2 after workup. Efforts to suppress formation of the coupled adduct (high dilution, Rh catalysis) were found to be unsuccessful. This may constitute a limitation on the range of substrates for the intramolecular hydrosilylation. Current efforts are focused on the use of homoallylic alcohols and chiral platinum catalysts.

Scheme 4



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