Account / Revue

Reactivity of silylated vinyloxiranes and silyl butene diols with palladium(0)

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Abstract

We review here our recent work on the reactivity of silylated vinyl epoxides as well as silylated butenediol derivatives in the presence of palladium(0) complexes. Silicon and its substituents play a major role in these reactions combining steric and electronic effects that could lead to special reactivities. ***To cite this article: C. Courillon et al., C. R. Chimie 7 (2004)***.
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Résumé

Nous avons réuni dans cet article nos travaux récents concernant la réactivité de petites molécules silylées dans des transformations catalysées par le palladium(0). Nous mettons en évidence les effets particuliers, stériques et/ou électroniques, du silicium sur la chimiosélectivité de la réaction et sur sa stéréosélectivité. ***Pour citer cet article : C. Courillon et al., C. R. Chimie 7 (2004)***.
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1. Introduction

Organosilicon compounds are versatile and powerful reagents in the field of organic synthesis [1–3]. Moreover, silanes have attracted considerable attention not only as biologically acceptable analogues of natural products [4–7], but also because silicon acts as a directing atom that increases [8–10] or reverses selectivities usually observed for the carbon analogues [11,12]. Recently, organosilanes have been extensively studied in cross-coupling reactions catalysed by palladium [13–15]. For example, Tietze took advantage of the presence of a silicon group to direct the last step of a domino-Heck double cyclisation process [16]. On the other hand, Hirao et al. reported first, nearly two decades ago, that 1- or 3-trimethylsilylallyl acetates in the presence of a palladium catalyst could react regio- and stereoselectively with stabilized carbon nucleophiles giving the corresponding vinylsilanes as the only product [17].

We report here some aspects of the influence of silicon in palladium-catalysed reactions. Interestingly, parts 2.1, 2.2 and 3.1 describe the reactivity of silylated vinyloxiranes with the silicon either in the γ or the α position to the vinyl function. Silicon is shown also to bring chemoselectivity in the reactivity of silylated butene diols and some interesting examples of synthetic applications are selected to illustrate the silicon effects in small substrates engaged in palladium-catalysed transformations.

2. Palladium-catalysed rearrangement of silylated vinyloxiranes

At the beginning of this project concerning the development of vinyloxiranes **1**, we intended to synthesize unsaturated amino acids **2** and this immediately raised the problem of the existence of three electrophilic carbons on the vinyloxiranes **1** that might react with a nitrogen nucleophilic species (Scheme 1).
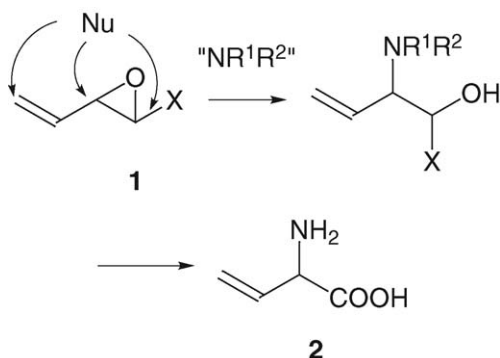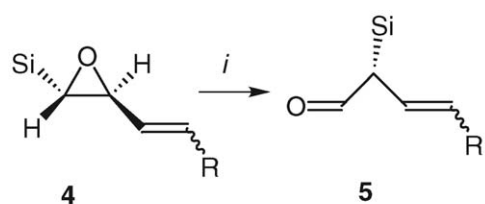

Scheme 1.
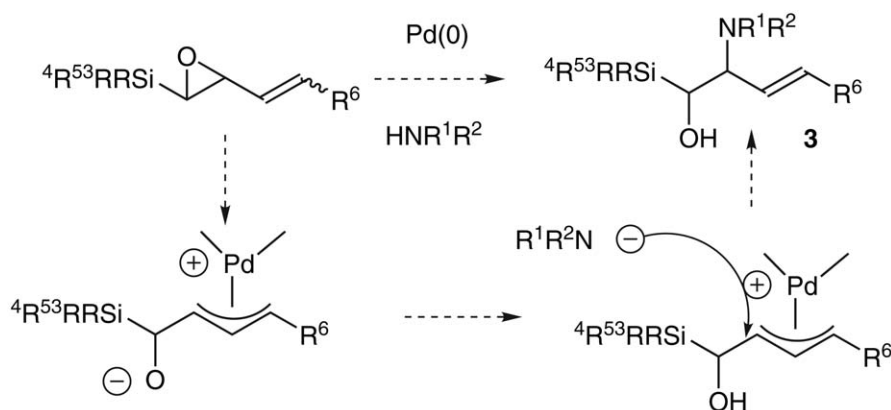
Trost [18] and Tsuji [19] had already shown that the regioselectivity of the palladium-catalysed nucleophilic addition on vinyloxiranes depended on the experimental conditions: the solvent, the ligands of the palladium, the temperature and the nature of the nucleophile. The choice of these conditions gave a 1,2- or a 1,4- selective addition of the nucleophilic species respectively on the proximal or the distal carbon centre of the π-allyl complex. Therefore, we decided to achieve the synthesis of the target compounds **2** via a palladium-catalysed key-step as well as to start with a vinyloxirane substituted by a silicon atom that might control the stereochemistry of the nucleophilic addition and also its regioselectivity since it might stabilize the positive charge on the β-carbon and favour the attack on the proximal carbon (Scheme 2).

We were not able to isolate any amino-alcohol **3** using phtalimide, which can give its acidic proton to the oxirane in the ring-opening reaction [20]. We obtained some aldehyde **5** instead, in a yield of 10%, which was increased when the reaction was conducted only with palladium(0) without any nitrogen reagent. Under these palladium-catalysed conditions, we therefore reported the first 1,2-shift of a silicon atom that occurred under smooth conditions (room temperature and neutral medium) [21] (Scheme 3).

2.1. Silylated vinyl-trans-oxiranes: general mechanistic study

This rearrangement reaction can follow two pathways after the formation of the π-allyl palladium complex **6**. One way goes through the formation of a

Scheme 2.

i : 5% Pd(OAc)₂, 20% P(O*i*-Pr)₃, THF, r.t.

Si = R¹R²R³Si

Scheme 3.

Scheme 4.

pentavalent silicon intermediate **7** and therefore yields the product of Brook rearrangement **8**, which is not really interesting. The second way is the migration of silicon, which has proven to occur *anti* to the palladium [22] and which gives the aldehyde **5** with a total chirality transfer and the retention of the configuration of the double bond [23]. The substituents of the silicon atom and the ligand of the palladium are directly responsible for the orientation towards the unsaturated enol ether **8** or the aldehyde **5** [24]. In order to favour the enantioselective rearrangement of compounds **4** into the aldehydes **5**, we reported the importance of having bulky groups on the silicon atom, namely dimethyl*tert*-butyl or tri*iso*propyl and of reducing the metal with π-acceptor ligands like triphenyl- or tri*iso*propylphosphite [24] (Scheme 4).

Our interest in this reaction is based upon the smooth experimental conditions, the short reaction times and the high degree of functionalization of the formed aldehydes. Indeed α-silylated aldehydes are difficult to isolate and to handle [25,26]. With the compounds **5**, we benefit from stable ambient molecules that may react on electrophiles by the double bond, with nucleophiles by the aldehyde moiety, and which may be oxidized in Tamao or Fleming transformations (Scheme 5).

Alkylation of the aldehydes **5** (reaction **a** of Scheme 5) has been thoroughly studied and gave interesting results in terms of diastereoselectivity, which will be developed in section 2.3 [27,28].

2.2. Scope and limits of the rearrangement reaction

In this part we show the influence of the structure of the starting silylated vinyloxirane on the rate of the rearrangement. The substituent on the double bond
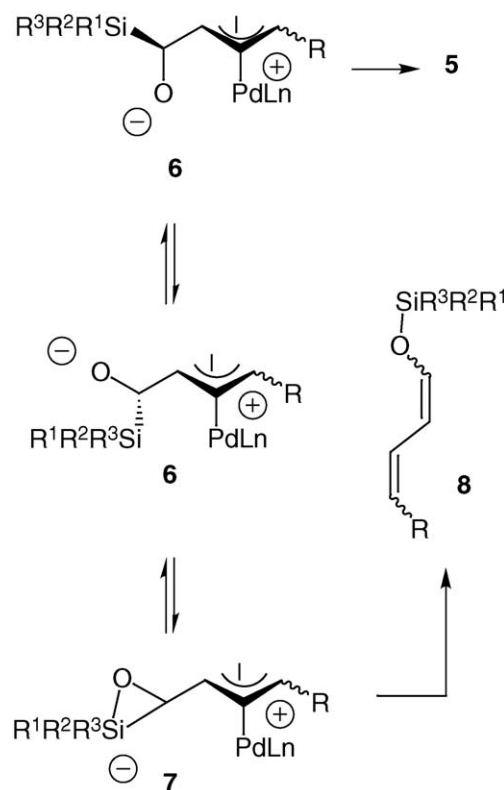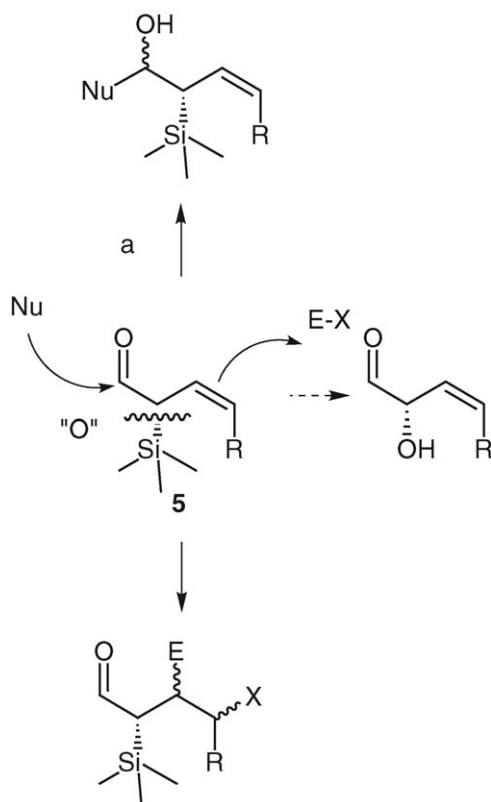
may accelerate the rearrangement, the configuration *cis* or *trans* of the epoxide plays as well a role in the rate and therefore in the choice of experimental conditions of the reaction. All these structural factors will be studied and rationalized in order to better understand the mechanism of this transposition reaction.

The first results in this field are shown in Table 1 with the *trans*-α,β-epoxy-δ-substituted-γ,δ-vinylsilanes **4a–e** that rearrange quickly into α-silylated-δ-substituted-γ,δ-unsaturated-aldehydes **5**.

The reaction conditions and the time of the reaction indicate that this rearrangement occurs easily and under smooth conditions. Compounds **4d–e** rearrange very rapidly on silicagel and need special basic conditions for their purification to avoid spontaneous migration of the silicon atom [29].
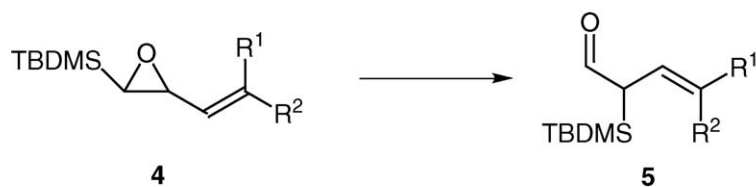
This reaction can provide α-silylated-β,γ-unsaturated-ketones when the silylated vinyloxiranes are substituted in the position α to the silicon atom. In this case the ketones **9a** and **9b** are formed in good yields and under similar smooth conditions [30,31] (Scheme 6).
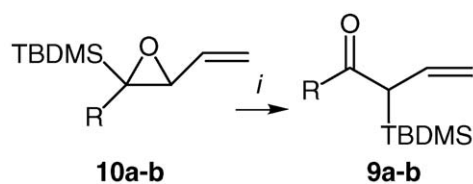
a

Scheme 5.

a : R = CH₃ 82% / **b** : R = PhCHOH 95%

i : Pd(OAc)₂, P(OPh)₃, THF, r.t., 2h

Scheme 6.

When the silylated vinyloxiranes display a quaternary allylic carbon in the β-position to the silicon atom, the experimental conditions of the rearrangement may be more drastic, as shown in Table 2 [29].

The degradation or the lack of reactivity in the case of vinylepoxysilanes **11c, 11e** or **11f** indicate the importance of the conformation of the oxirane in the rate of the rearrangement. Therefore, the double bond has been frozen into a cycle like in the epoxylactone **15** which reacted very easily in THF at room temperature with palladium(0) and gave the aldehyde **16** with a very good yield (Scheme 7) [29].

A limiting factor of the rearrangement reaction is probably the steric hindrance brought by the substitu-

Table 1

Quick rearrangement of *trans*-α,β-epoxy-δ-substituted-γ,δ-vinylsilanes **4a–e** into α-silylated-δ-substituted-γ,δ-unsaturated-aldehydes **5**.

4	R¹	R²	Temperature	Time	Yield (%)	Conditions
4a	H	H	r.t.	2 h	85	Pd(0)
4b	H	COOMe	45 °C	1 h	65	Pd(0)
4c	COOMe	H	45 °C	1 h	76	Pd(0)
4d	H	Ph	r.t.	5 min	98	SiO₂
4e	Ph	H	r.t.	5 min	98	SiO₂

Table 2

Experimental conditions of the rearrangement of compounds **11a–f** into compounds **12–14**.
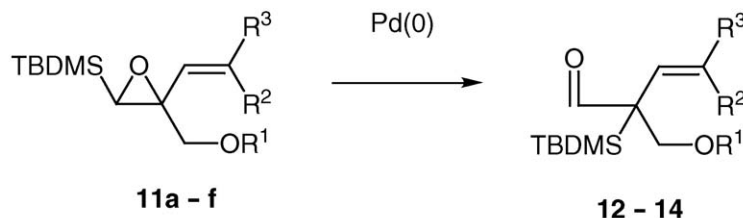
| Substrate	R^1	R^2	R^3	T (°C)	t (h)	Compound	Yield (%)
11a	CH_2Ph	H	H	r.t.	1	**12**	94
11b	TBDMS	H	H	r.t.	3	**13**	93
11c	CH_2Ph	COOMe	H	76	24	–	–
11d	TBDMS	COOMe	H	76	6	**14**	91
11e	CH_2Ph	COOMe	Et	76	24	–	–
11f	TBDMS	COOMe	Et	76	24	**11f**	quant.
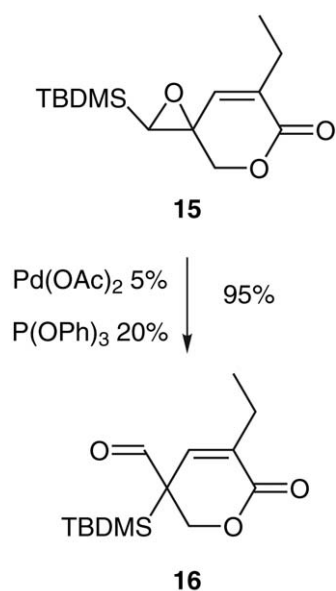
Scheme 7.

ents on the quaternary carbon atom. In the case of the trisubstituted olefins **11e** and **11f**, this steric factor prevents the double bond from lining up with the epoxide, the palladium can still bind to the vinyl group but there is not the planarness required for the formation of a π-allyl complex. This factor is less important in the case of unsubstituted olefins. In the case of the cyclic compound **15**, the blocked conformation of the double bond imposes this planarness and allows easily the occurrence of the rearrangement in a good yield. Formation of palladium π-allyl complex **E** can only derive from the palladium-associated-form **D** that exists only if the steric hindrance between the double bond and the ether function is sufficiently low (Scheme 8).

Indeed this 1,2-silicon migration proves to be a versatile tool in the field of synthetic chemistry with some limits due to the steric hindrance of some β-disubstituted-α,β-epoxy-γ,δ-vinylsilanes.

2.3. Synthetic applications

This palladium-catalysed rearrangement of silylated vinyloxiranes was associated in a one-pot proce-

Scheme 8.

e.e. = 93-99% d.e. = 75-98%

R = Me, *i*-Pr, *t*-Bu, C$_5$H$_{11}$, C$_{11}$H$_{23}$,

HC≡— , ⌇⌇
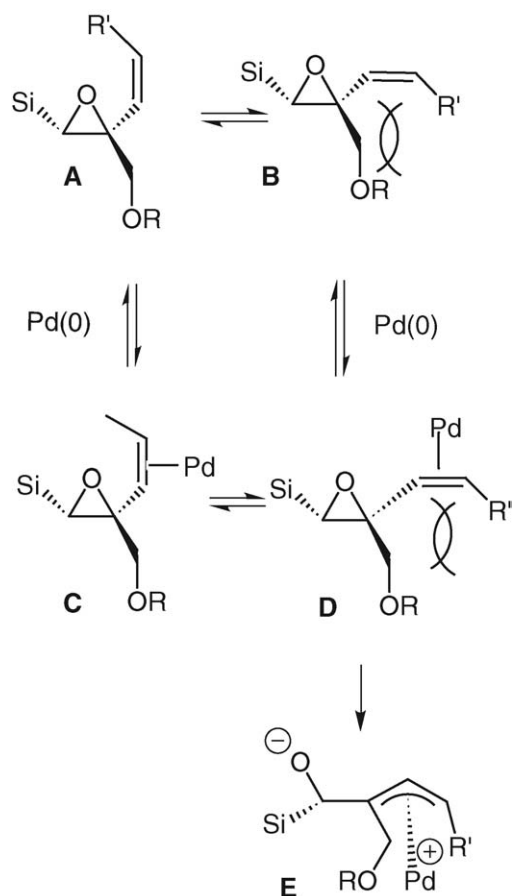
Scheme 9.

dure with the alkylation of the aldehydes **5** that has been thoroughly studied and gave interesting results in terms of diastereoselectivity [27]. When the starting oxirane has a *Z* double bond substituted by an electron-withdrawing group as a methyl ester, alkylation gives an intermediary alcoolate that can cyclise into a δ-lactone [32] (Scheme 9).

These highly functionalized lactones are efficient Michael acceptors that undergo conjugated additions and further electrophilic trapping with a high diastereoselectivity. When the electrophile is prochiral like the benzaldehyde, there is even an extracyclic stereogenic carbon atom whose configuration is controlled in the process of the trapping [33,34] (Scheme 10).

Tetrasubstituted δ-lactones **18** can be prepared from compound **17** in four steps accomplished in a one-pot procedure with formation of four contiguous stereogenic carbon atoms in good yield [33].
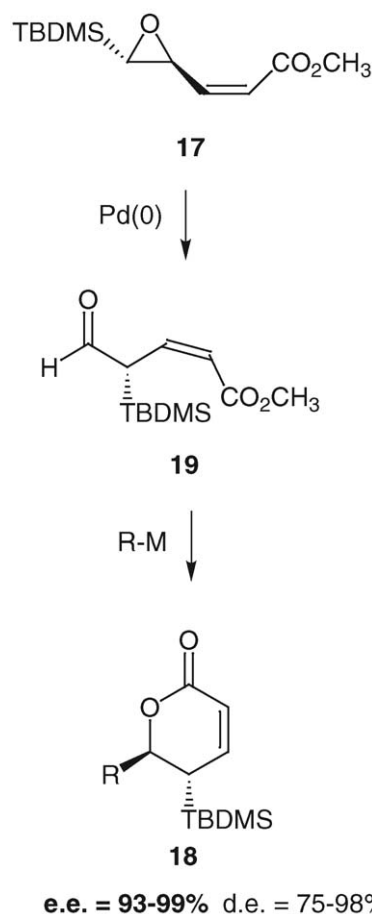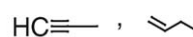
These results confirm the efficiency of the palladium-catalysed rearrangement of α,β-epoxy-γ,δ-vinylsilanes in the field of organic synthesis in terms of stereoselectivity and high functionalisation.

3. Silyl-substituted 1,4-butadienol derivatives and palladium-catalysed alkylations

3.1. α′,β′-vinyl-α,β-epoxysilanes

During our study on the behaviour of a malonate derivative **19a** bearing a vinylepoxide moiety, we observed a stereoselective 4-*exo-trig* cyclisation leading
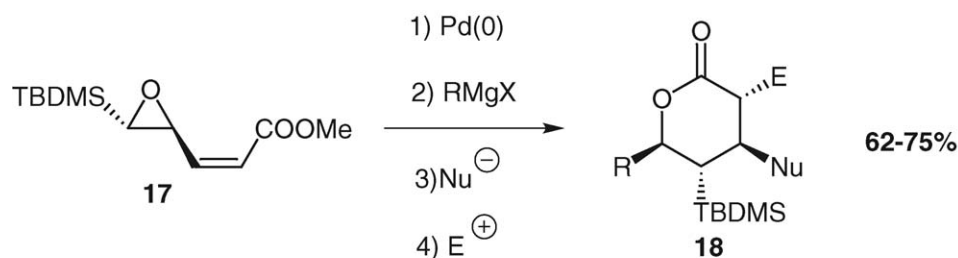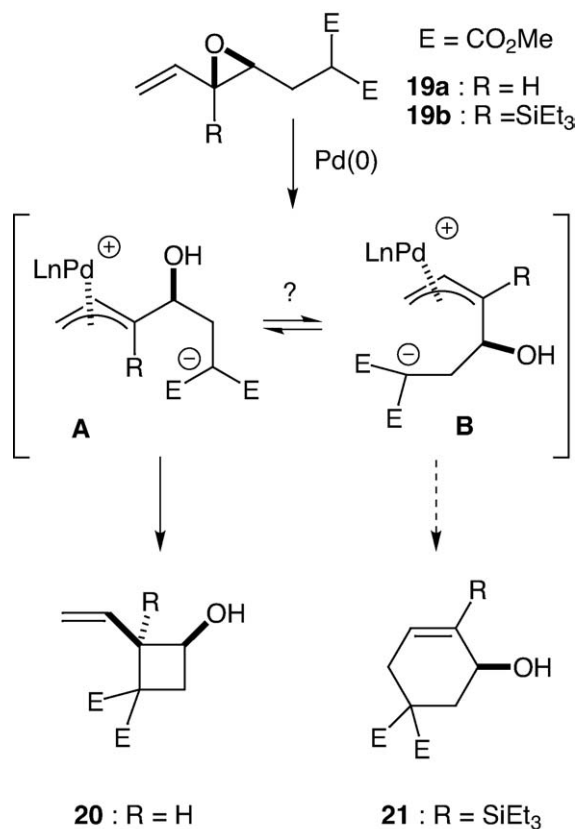
Nu = *n*-Bu, CH=CH(CH$_2$)$_2$CH$_3$, CH$_2$Ph, SBu, SPh, SPhOMe

E = CH$_2$=CHCH$_2$-, CH$_3$CO-, PhCHOH-, CH$_3$-

Scheme 10.

to the corresponding cyclobutanol **20** in 70% yield (Scheme 11). In order to check the possibility to reverse the chemoselectivity of the reaction, we decided to prepare a silylated substrate **19b**. Indeed, based on the previous work of Corriu [35], Trost [18], Tsuji [36],
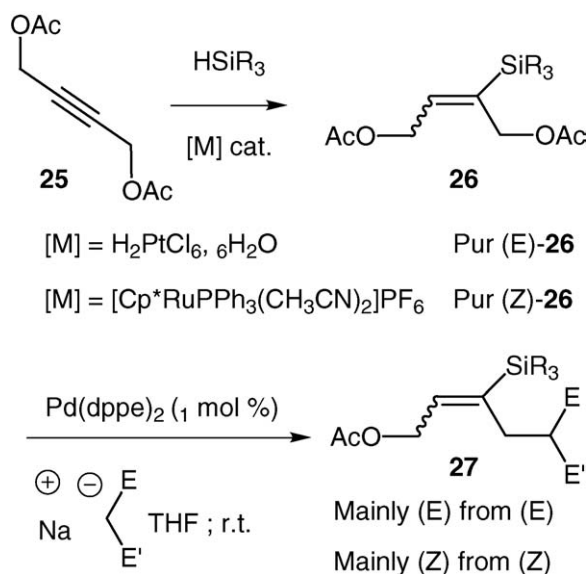

Scheme 11.

Sato [37] and others [9], silicon atom in one of the terminal positions of a π-allyl palladium complex plays a curious role. Thus, attacks by nucleophiles occur at the remote position with respect to the silicon even if a bulkier substituent is present [9,38]. Starting from vinylsilane **19b**, the attack of a palladium(0) species should afford the zwiterionic π-allylpalladium intermediates **A** and/or **B** (Scheme 11). The presence of a silicon group should favour the formation of the cyclohexenol **21**, since steric and electronic factors act in the same direction.

On the other hand, having already observed silyl migration with vinyl epoxides **5** (vide supra), we first investigated the reactivity of the 2-triethylsilyl vinyle-poxide **22** in the presence of palladium catalyst and dimethylmalonate as nucleophile (Scheme 12) [39]. Two products are isolated after 4 h. The expected one **23** in a low yield (11%) as well as a second one **24**, in 16% yield, resulting from a 1,2 C-to-O silyl migration, followed by the addition of the dimethyl malonate
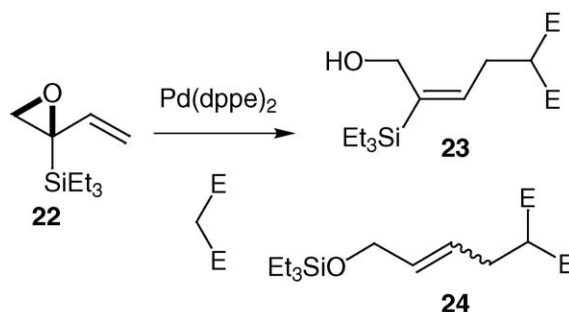
Scheme 12.

Scheme 13.

anion (Scheme 12); C-desilylation during palladium-catalysed alkylation has been reported [40].

3.2. Chemo- and stereoselective alkylations of 2-silylbut-2-ene diol derivatives

With the precedent experiment we have shown that 2-triethylsilyl vinylepoxide underwent a migration of the silicon group from carbon to oxygen during palladium-catalysed reactions. However, in order to validate our strategy where a silicon group would control the chemo- and stereoselectivity of palladium-catalysed reactions, we prepared a C4 analogue of our desired silylated vinylepoxide (Scheme 13). In this context, we chose a general synthesis that could give access to different silyl substituted C4 synthons from commercially available cheap materials. Our approach started with the 2-butyne-1,4-diol diacetate **25** (easily prepared by diacetylation of 2-butyne-1,4-diol). Stereoselective *syn* or *anti* hydrosilylation could be

achieved in high yields by choosing either platinum or ruthenium complexes as catalyst [41,42]. The obtained vinylsilanes **26** present two potential leaving groups that are differentiated only by their position relative to the silicon group. We have shown that in the presence of catalytic amounts of palladium (0) complexes, alkylations, with stabilized carbanions as nucleophiles, occurred in good to excellent yields (70–100%). Gratifying, the silicon group totally differentiated the two potential leaving groups: only the β-acetate relative to the silicon was displaced. In addition, very high stereoselectivities were observed. The stereoselectivity was dependent on the temperature of the reaction but in all the substrates studied, the configuration of the double bond was mainly retained starting either from *Z* or *E* **26** (Scheme 12). As an example, using dimethyl malonate as nucleophile, the *E/Z* ratio of **27** is varying from 25:75 at r.t. to 10:90 at 0 °C, starting from *Z*-**26**, whereas it is varying from 90/10 to 98/2 starting from *E*-**26**.

The allylation of dimethyl malonate was performed with the same efficiency with variously substituted *(E)*-vinylsilanes **26** and some representative examples are reported in Table 3.

The preparation and reactivity of two analogues in which the silyl group has been replaced by a *tert*-butyl group were also examined. Their lower reactivity toward the nucleophile as well as the lost of stereoselectivity can be ascribed to the ability of the silicon group to stabilize a β–carbocation. Our interest in the use of these bis–allylic substrates was originally stimulated when we discovered the behaviour of a dissymmetric precursor **28** bearing a carbonate in place of the acetate in the γ position relative to the silicon (Scheme 14). With either dimethyl malonate or methyl acetoacetate sodium salts, acetate acts as the leaving group, in spite of the recognized better ability of carbonates as leaving groups in this type of chemistry [43,44].

As a representative example, dimethyl malonate gave respectively the β and γ adducts in a ratio of

Table 3

Representative examples of the he allylation of dimethyl malonate with variously substituted (*E*)-vinylsilanes **26**

Entry	Substrate	SiR$_3$	Vinylsilane (%)	*E/Z* ratio
1	**26a**	SiEt$_3$	95	98/2
2	**26b**	Si(*i*-Pr)$_3$	75	97/3
3	**26c**	SiMe$_2$*t*-Bu	98	100/0
4	**26d**	SiMe$_2$Ph	98	100/0
5	**26e**	SiMe$_2$(4-MeO–C$_6$H$_4$)	82	95/5
6	**26f**	SiMe$_2$(4-CF$_3$–C$_6$H$_4$)	64	98/2
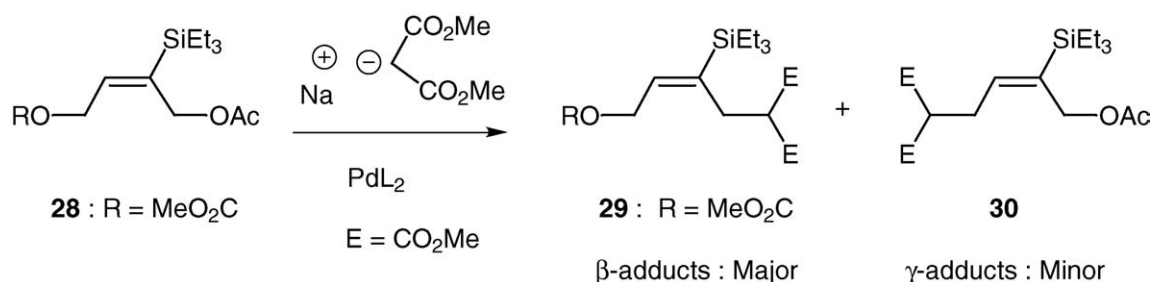
Scheme 14.

80:20. Some theoretical calculations have been done and, as expected, have shown that the presence of silicon in the central carbon atom of π-allyl palladium cations causes stronger Pd–allyl interaction, therefore justifying that cations **31a** and **31b** are more stable than their isomers **32a** and **32b** possessing a silicon at the terminal atom (Scheme 15) [45].

3.3. Competitive 5-endo-trig vs 3-exo-trig palladium-catalysed cyclisations. Preparation of cyclopentenes

The described silylated allylic diacetates still present a leaving group after reaction with nucleophiles. Moreover, after reaction with malonates, the products **27** are themselves nucleophiles due to the acidic hydrogen of the malonate function. Treatment with sodium hydride followed by addition of palladium catalyst gave after one night at reflux the expected cyclopentenes **33** in good yields as the unique product (Scheme 16). No trace of the corresponding cyclopropane could be observed [46]. Varying the silyl substituents from alkyl to aryl was dramatic for the course of the reaction. Alkyl groups are tolerated and

allowed the formation of the expected cyclopentene, whereas aryl one totally inhibits the cyclisation [47]. We thus have confirmed that silyl group at a proper position can drive palladium-catalysed cyclisation to the 5-*endo-trig* process. Balance has to be found between the substituents of the silicon as well as the size and the basicity of the internal nucleophile. Indeed, when the keto-ester function is the nucleophile, competitive hetero-5-*exo-trig* cyclisation occurs and dihydrofuran derivatives were isolated in 69% yield.

### 3.4. Competitive 5-exo-trig vs 7-endo-trig cyclisations. Preparation of pyrrolidones

In 1998, G. Poli et al. prepared 3,4-disubstituted pyrrolidones in high yields by a palladium-catalysed cyclisation based on the interaction between a resonance-stabilized carbanion and an allylic acetate function, tethered by a nitrogen atom [48]. Having successfully prepared cyclopentenes by a 5-*endo-trig* palladium-catalysed reaction, we started a project to study the effect of silicon on these kinds of molecules. In particular, we were curious to verify if such modifications could still permit cyclisations, and, in positive
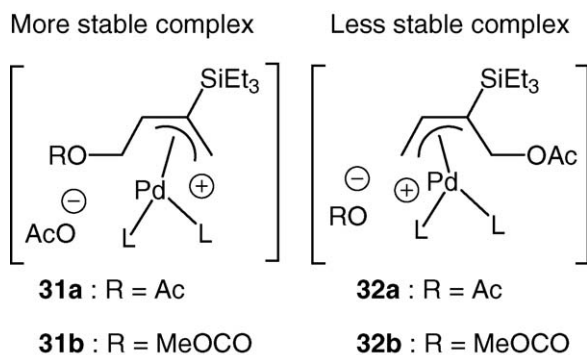
Scheme 15.
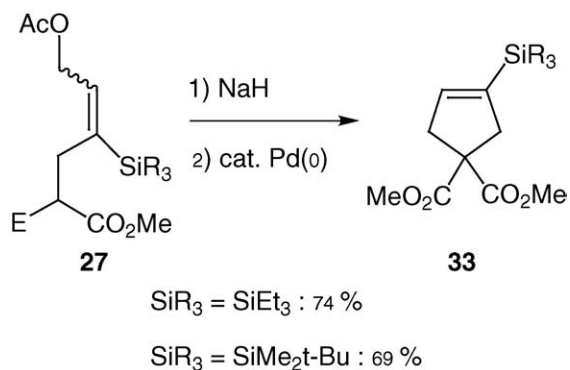
Scheme 16.
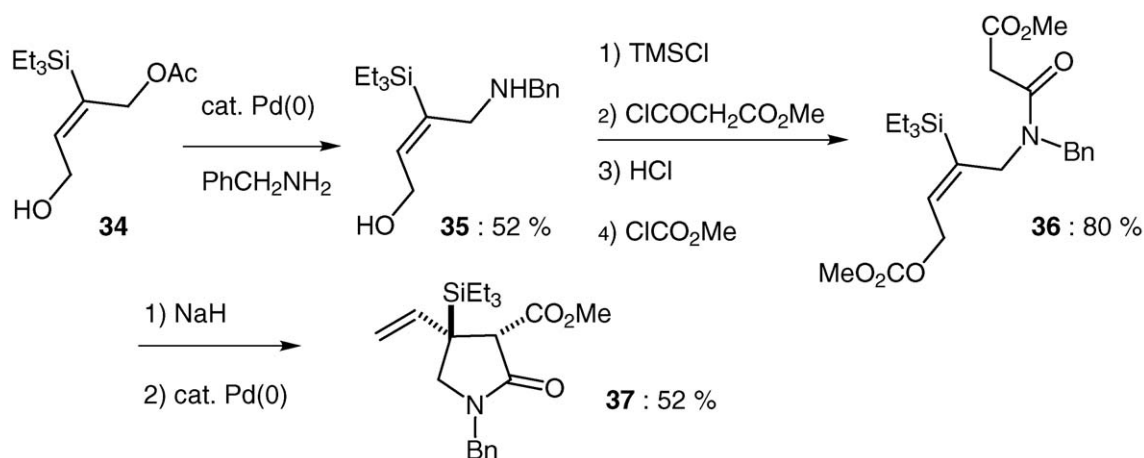
Scheme 17.

case, to determine a possible 5-*exo versus* 7-*endo* preference. The precursors have been prepared from the 1,4-butyne diol by first monoacetylation followed by a regioselective platinum-catalysed hydrosilylation giving **34** in 80% yield. A palladium-catalysed reaction with benzylamine afforded in 52% yield the expected aminoalcohol **35** bearing the amine function at the less substituted carbon (Scheme 17). Some additional steps delivered the acyclic precursor **36** bearing the triethyl-silyl group.

Treatment of the sodio enolate of compound **36** with 5 mol% Pd(OAc)$_2$ and 10 mol% of dppe in DMF at 100 °C for 30 min gave the pyrrolidone **37** as the unique product in 52% yield [49]. Exclusive formation of pyrrolidone structures from the above amide precursor indicates that a 7-*endo* type approach is in this case forbidden. Such a phenomenon, which contrasts with what was observed with the related β-ketoesters [50], is certainly associated with the amide bond. Indeed, the nature of such a function is expected to force the C–C(O)–N–C dihedral angle value of the reacting cyclisation precursors toward a planar arrangement (0° or 180°), thereby disfavouring the 7-*endo* cyclisation [51].

4. Conclusion

This paper has summarized the results acquired by us in the field of silylated oxygenated molecules. We pointed out that substituents on the silicon atom of the γ,δ-vinyl-α,β-epoxysilanes could direct the reaction towards a Brook rearrangement or an enantioselective 1,2-carbon-to-carbon silyl migration. We described the silicon effects in the chemoselectivity of Pd-catalysed alkylations on different substrates like α,β-vinyl-α,β-epoxysilanes or silylated butene diols. Finally, we stressed the point of synthetic applications with the preparation of highly functionalized δ-lactones and easily accessible cyclopentenes.

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