

## Synthetic methodology involving the carbopalladation of allenes

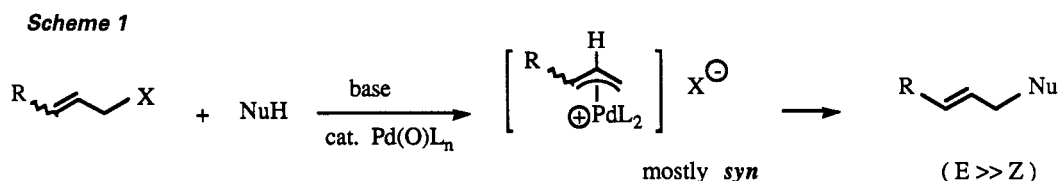
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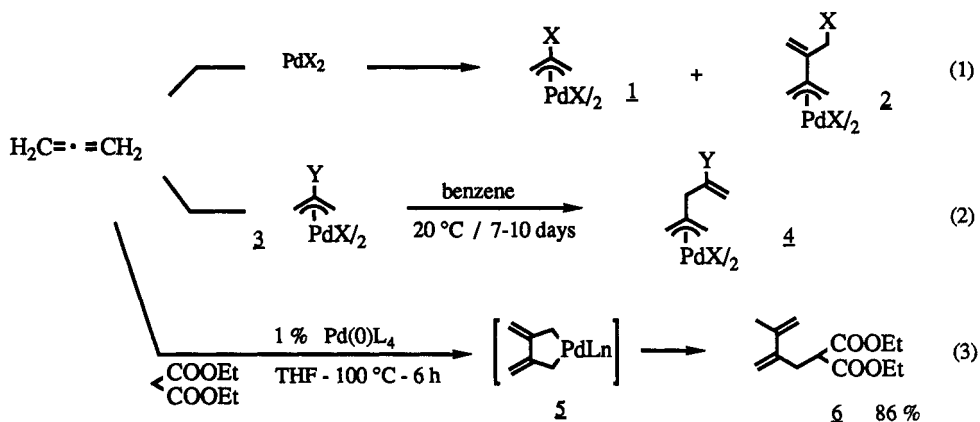
**Abstract** - Carbopalladation of allenic compounds by vinylic or aryllic palladium species [vinylic or aryllic halides + Pd(0)L<sub>n</sub> catalyst] affords new 2-substituted π-allyl palladium complexes. These intermediates show interesting stereochemical properties due to the conjugated unsaturated system on the central carbon atom of the η<sup>3</sup>-allyl ligand and react with high regio and stereoselectivities with delocalized carbonnucleophiles. The overall palladium(0)-catalyzed process realizes the creation of two new carbon-carbon bonds in a single reaction and leads to functionalized 1,3-dienic (or styryl) compounds of known stereochemistry. This three component reaction is the basis of a straightforward access to valuable unsaturated synthetic intermediates. Applications of this methodology to the synthesis of unsaturated α-aminoacids, dienyilsilanes, vinylcyclopentenes or cyclopropanes and steroids will be given.

### INTRODUCTION

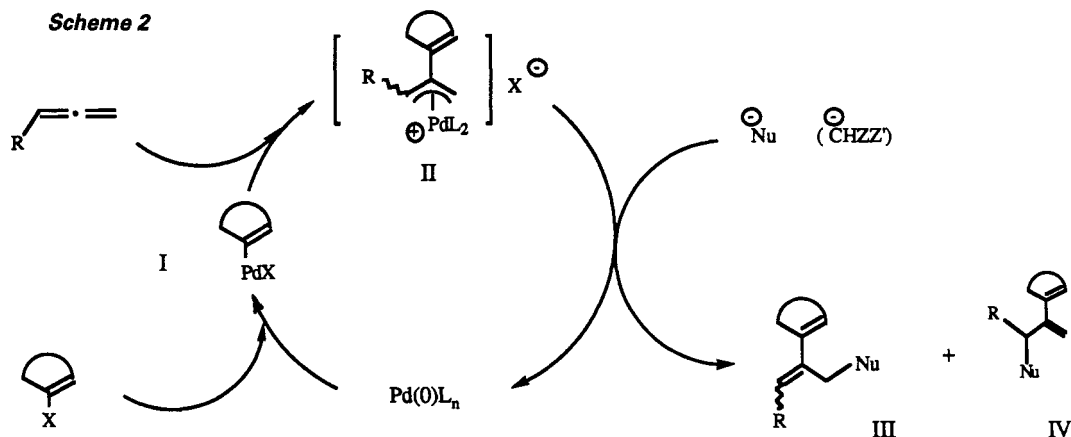
The 1,2-dienic unit of allenes has for a long time seemed an attractive synthetic functionality because of the specific stereochemical features of its two orthogonal cumulated double bonds and the associated reactivity (ref. 1). Numerous preparative methods to these compounds, functionalized or not, are now available (ref. 1) and on-going research in this field is focusing on their potential utility as synthetic building blocks. Our search toward new applications of allenic compounds led us to seek a palladium-promoted procedure which would afford a new route to π-allyl complexes. For two decades this chemistry has been largely developed as a synthetic tool for the highly regio and stereoselective allylation of nucleophiles (scheme 1) (ref. 2-4) :



Two such processes starting from allenes have already been disclosed as stoichiometric reactions. Addition of a palladium salt to allene may lead to two organopalladic species **1** and **2** according to the reaction conditions (eq. 1) : heteropalladation of allene leads to complex **1** whereas the formation of complex **2** clearly involves an oxidative dimerization of allene (ref. 5). Addition of some organopalladic complexes, mostly π-allyl, has been performed as well (eq. 2) (ref. 6), but very few synthetic works using this seemingly easy addition of organopalladic species to an allenic unit have been described. Furthermore, they involved stoichiometric amounts of the transition metal (ref. 7). More interesting in this respect was the pioneering work of Coulson who obtained malonate **6**, presumably via complex **5**, through dimerization of allene (eq. 3) (ref. 8).



With these ideas we designed a catalytic cycle which led us to imagine the formation of conjugated  $\pi$ -allyl complexes through a cross-condensation between an allene and an unsaturated (vinylic or aromatic) halide (scheme 2). The oxidative addition of this halide to a Pd(0) complex would first generate a  $\sigma$ -organopalladic species I. A second step, namely the carbopalladation of the allenic compound, would involve the insertion of the allenic compound in the complex I and give the unsaturated  $\pi$ -allyl complex II; finally, reaction of an appropriate carbonucleophile would afford a functionalized dienic (or styryl) compound III (and/or IV according to the regioselectivity of this last step) together with the catalytic palladium complex.

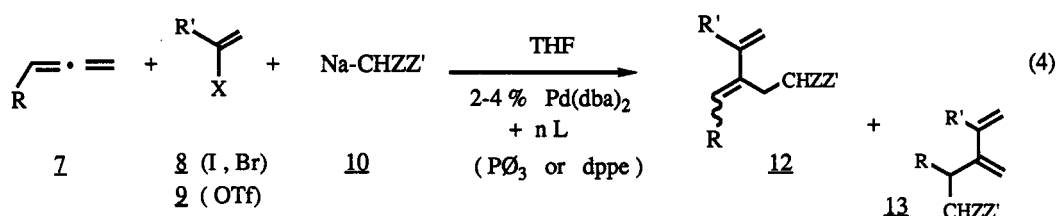


This overall palladium-catalyzed process involves the formation of two carbon-carbon bonds in a single reaction, and would set up a fruitful valorisation of allenic compounds as synthetic intermediates. We report here on the development of this reaction and several synthetic applications of this methodology.

## I CARBOMETALLATION OF ALLENES: SYNTHESIS OF FUNCTIONALIZED DIENES

Our efforts were devoted to the search of catalytic conditions for such a palladium-promoted reaction together with the study of the reactivity of the new unsaturated  $\pi$ -allyl palladium intermediates II. These last complexes present an a priori conjugated double bond in the 2-position which may influence the regio and stereoselectivity of their reactions with nucleophiles.


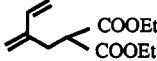

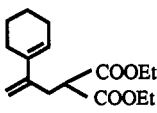

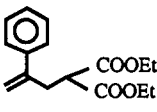

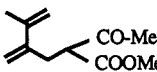

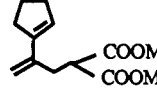

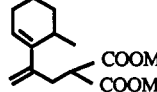

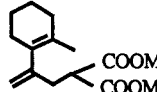
Thus, we have found that a zerovalent palladium catalyst Pd(0)L<sub>n</sub> does catalyse the reaction of an allenic hydrocarbon **7** with a vinylic (or aromatic) halide **8** and the anion of a malonic type compound **9**, and affords highly regioselectively a functionalized diene **12** (eq. 4) with a very small amount (or none at all) of the regioisomer **13** (ref. 9,10).



Tetrakis(triphenylphosphine) palladium and several catalytic systems, prepared "in situ" from bis(dibenzylideneacetone)palladium Pd(dba)<sub>2</sub> and several equivalents of an aromatic phosphine, effectively catalyzed the reaction in THF but the most efficient one was obtained from Pd(dba)<sub>2</sub> and one equivalent of (diphenylphosphino)ethane (dppe). The reaction was carried out under an inert gas (nitrogen or argon) at 45-65 °C during 24-50 hours according to the substitution patterns of the allenic and vinylic substrates. Reactions with volatile compounds (allene, vinylbromide,...) needed to be performed in an autoclave.

Tables 1 and 2 gather some of the results obtained from allene and 1,2-decadiene associated with different unsaturated halides; yield of diene **12** was the range 60-90% and in the case of the monosubstituted allene, regioselectivity was higher than 95% for this regioisomer **12**. Enol triflates **2**, which are easily available from ketones, can be used as the vinyl components as well. Their use greatly expands the synthetic applications of the procedure (ref. 11).

TABLE 1. Synthesis of functionalized dienic compounds **12**.

Run	vinyl derivative	Nucleophile	<b>12</b>	isolated yield
1	$\text{H}_2\text{C}=\text{C}=\text{CH}_2$ 	$\begin{array}{l} \text{COOEt} \\ \text{COOEt} \end{array}$		60%
2		"		84%
3		"		82%
4		$\begin{array}{l} \text{CO-Me} \\ \text{COOMe} \end{array}$		90%
5		$\begin{array}{l} \text{COOMe} \\ \text{COOMe} \end{array}$		75%
6		"		74%
7		"		65%

\* Reactions of enol triflates were carried out in DMSO, with 2.5 equiv. of LiCl to the catalyst Pd(dba)<sub>2</sub> + 4 Pφ<sub>3</sub>

### Stereoselectivity

The stereoselectivity was found to be slightly dependent on the nature of solvent (THF, DMSO, CH<sub>3</sub>CN or DMF) and the temperature of the reaction (between 40 and 100 °C). However, it clearly depends on the steric hindrances of the vinylic component and of the nucleophile. Table 2 demonstrates that unhindered vinylic bromides (run 1,2) lead to about equal amounts of the two stereoisomers (E)-**11** and (Z)-**11**; but dienes **11E** are highly stereoselectively obtained from larger vinylic derivatives (run 3,4 and 5). Table 3 compares the results obtained from 1,2-decadiene and two different vinylic bromides **8** (R' = H or CH<sub>3</sub>) associated with several nucleophiles; a bulky nucleophile favors the formation of the (Z)-**11** stereoisomer and the stereoselectivity may even be reverse with vinylbromide associated with the anion of a Schiff base.

TABLE 2. Stereoselectivity

Run		Na-CHZZ THF / 65 °C / 48 h 4 % Pd(dba) <sub>2</sub> + dppe		E / Z	yield
1				53 / 47	75 %
2				56 / 44	80 %
3				100 / 0	85 %
4				86 / 14	63 %
5				85 / 15	71 %

R = nC<sub>7</sub>H<sub>15</sub>, Z = COOEt

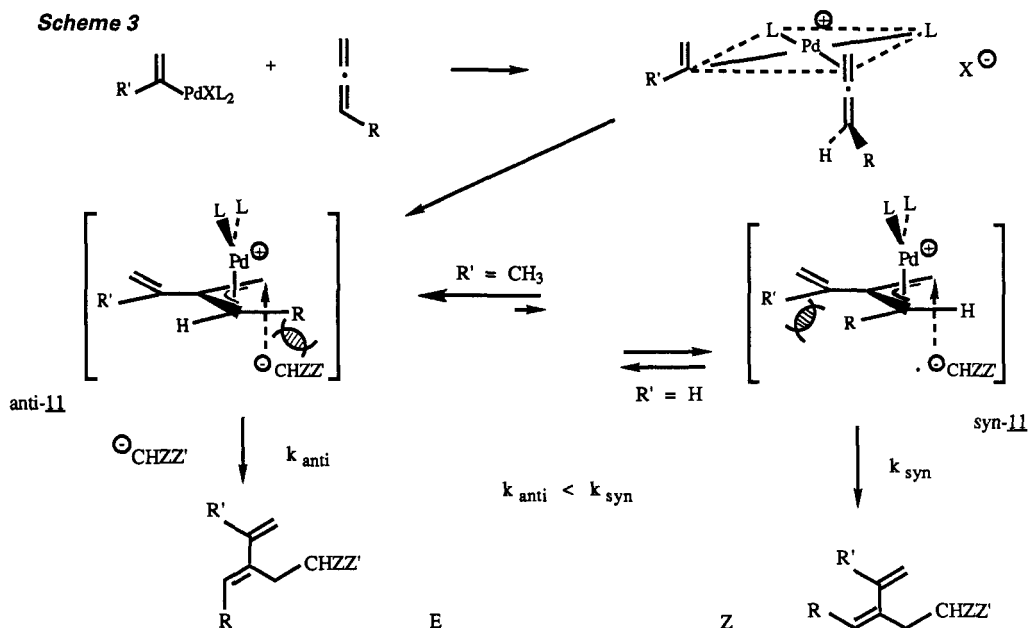
TABLE 3. Stereoselectivity dependence on vinylic halide and nucleophile

		Pd(dba) <sub>2</sub> + dppe		THF - 65 °C		CHZZ'	
H <sub>15</sub> C <sub>7</sub>		R' = CH <sub>3</sub>		R' = H			
		E / Z		E / Z		(E)- <b>12</b>	(Z)- <b>12</b>
		100 / 0	85 %	53 / 47	75 %		
		99 / 1	78 %	27 / 73	74 %		
		80 / 20	57 %	30 / 70	71 %		
		75 / 25	52 %	15 / 85	43 %		

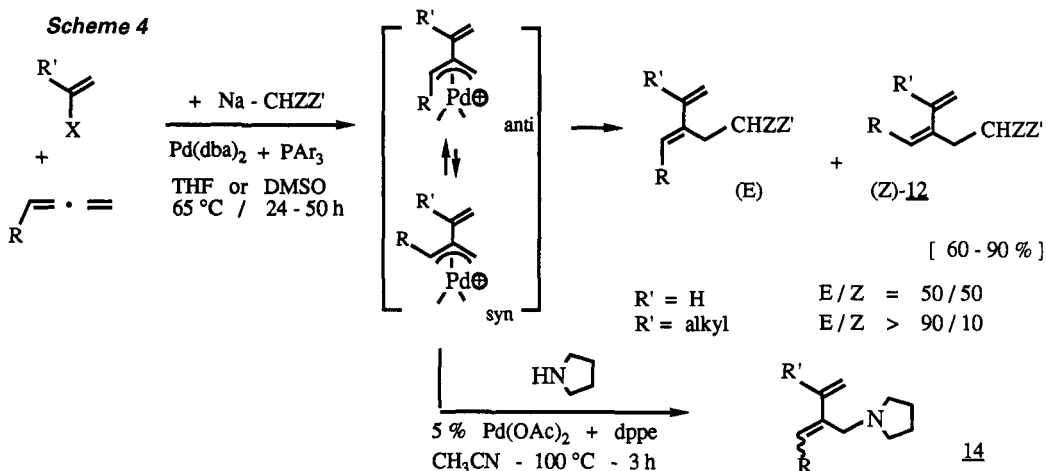
### Mechanism

These stereoselectivities can be explained by evaluating the relative stability of the two anti and syn  $\pi$ -allyl palladium intermediates **11** (assuming the coplanarity of the vinylic double bond with the  $\pi$ -allyl system) and the relative rates of reaction of nucleophiles **10** with the intermediates **11**. Thus, a likely rationalization is as follows (scheme 3): coordination of allene **7** to the initial  $\sigma$ -vinylic palladium species **I** would generate a

$\pi$ -complex; insertion of the allene would then occur through the less hindered half-space defined by the allenic unit and would lead kinetically to the anti-11 complex. When R' is an alkyl group this complex would also be the thermodynamic one, because of minimized steric interactions between the R and R' group; reaction of the nucleophile would then give diene (E)-12 with a high stereoselectivity. If R' is an hydrogen atom, the isomerisation of the anti-11 to the syn-11 complex would take place; their similar thermodynamic stabilities explain the formation of about an equal mixture of the two (E) and (Z) stereoisomers 12. A kinetic effect which diminishes the nucleophilic attack of large delocalized anions 10 with the anti-11 complex, because of steric interactions between the R group and these nucleophiles, may account for the reverse stereoselectivities encountered in these cases.



Thus, the three-component reaction between an allene, a vinylic derivative and a delocalized anion in the presence of a Pd(0) catalyst provides an easy and relatively mild stereoselective access to functionalized dienes 12 which is summarized in scheme 4. A related synthesis of dienic amines 14 which involves an identical catalytic scheme and the use of pyrrolidine as the nucleophile has also been described by Tsuji's group (ref. 12).



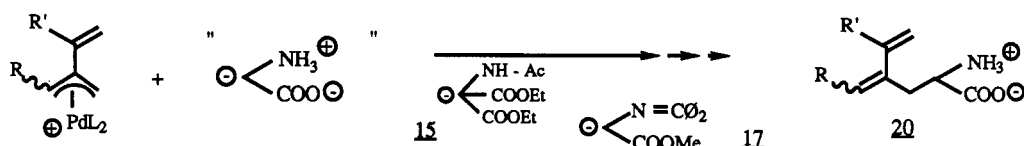
These complementary works show the synthetic utility of the carbopalladation of allenes to generate  $\pi$ -allyl palladium complexes which are substituted by an unsaturated group in the central position. With such a conjugated substituent, complexes 11 may be more stable in the anti configuration, anti-11 (R' = alkyl), which

is the reverse situation when compared to the one mostly encountered with  $\pi$ -allyl complexes (see scheme I). These stereochemical features are the basis of the stereoselective synthesis of dienes described here. Several applications of this carbopalladation procedure, which involve a straightforward access to functionalized unsaturated intermediates and their subsequent transformations, will illustrate this methodology.

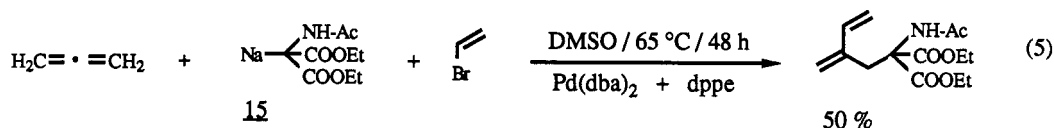
## II SYNTHESIS OF DIENIC $\alpha$ -AMINO ACIDS

Increasing interest has been recently devoted to the synthesis of non proteinogenic unsaturated  $\alpha$ -amino acids because of their potential biological activities, especially as suicide enzyme inhibitors (ref. 13). The presence of an extra, ethylenic, acetylenic or allenic unsaturation has been found to notably modify the biological properties of these amino acids. The methodology described above seemed quite suitable for the synthesis of a new class of unsaturated  $\alpha$ -amino acids which possess a 1,3-dienic functionality (scheme 5). Among the possible anionic precursors equivalent to the anion of glycine, the anions of acetamidomalonate **15** and the Schiff base **17** derived from methylglycinate were tested.

Scheme 5

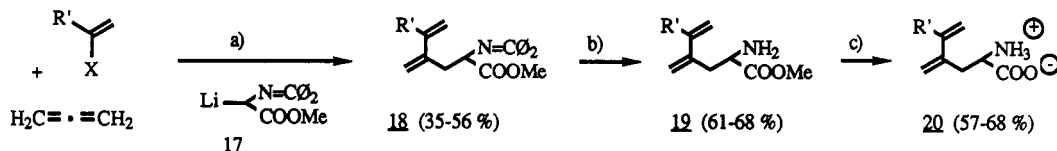


Reaction of allene with vinyl bromide and diethylacetamido malonate **15**, in the presence of 5 % molar of  $\text{Pd}(\text{dba})_2 + \text{dppe}$ , gives a new dienic acetamidomalonate **16** with a moderate 50 % yield (eq. 5). However, the acid hydrolysis (6N HCl, MeOH, reflux) giving the free  $\alpha$ -amino acid met with little success, presumably because of the high sensitivity of the dienic pattern toward the acidic conditions.



The anion **17** of the Schiff base derived from methylglycinate, which was formerly shown to be a good nucleophile in Pd(0)-catalyzed allylic alkylation (ref. 14), was successfully introduced in our reaction; this allowed the preparation of several dienic amino acids according to scheme 6 (ref. 15).

Scheme 6



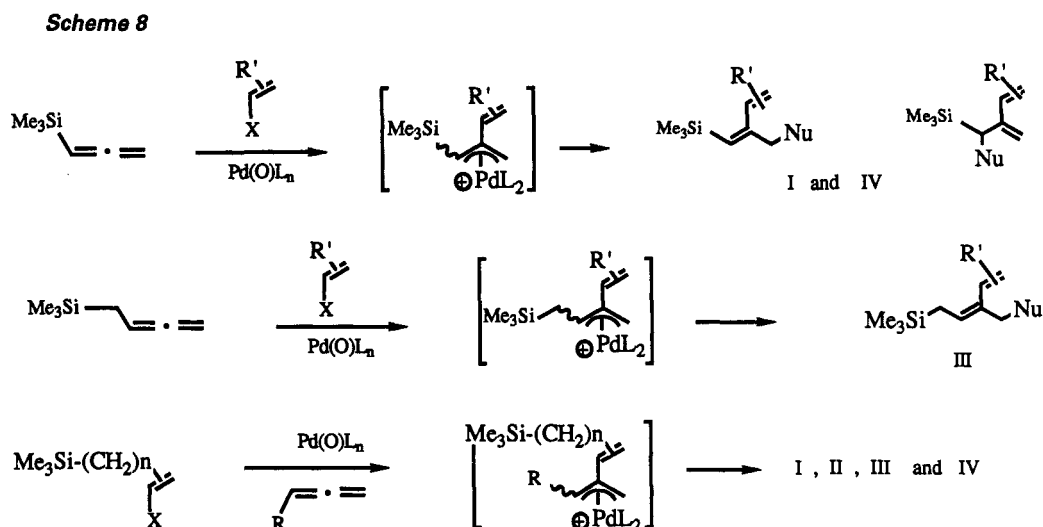
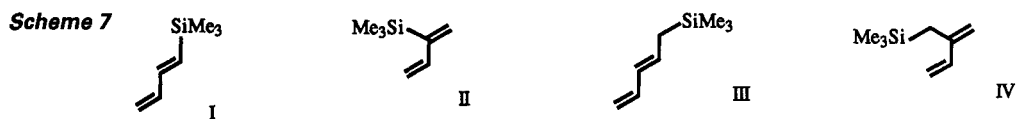
- a) 4 %  $\text{Pd}(\text{dba})_2 + 1 \text{ dppe}$ ; THF /  $55-60^\circ\text{C}$  / 24 h    b) 2N HCl -  $20^\circ\text{C}$  - 30 min  
c) 1N NaOH / MeOH -  $20^\circ\text{C}$  - 2 h (ion exchange chromatography).  $\text{R}' = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5, (\text{cyclohexenyl})$

Imino esters **18** were then obtained with a 35-56 % yield. Their hydrolysis to amino esters **19** were carried out under mild acidic conditions; subsequent saponification and acid ion exchange chromatography afforded pure dienic  $\alpha$ -amino acids **20** (57-68 %).

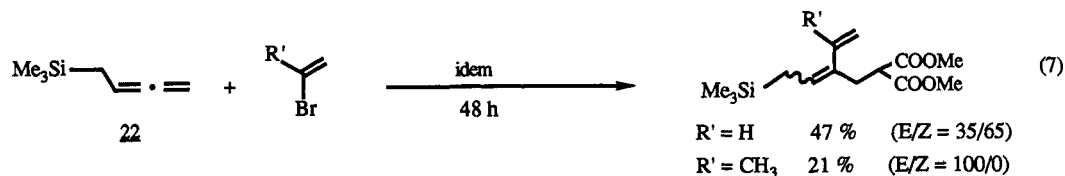
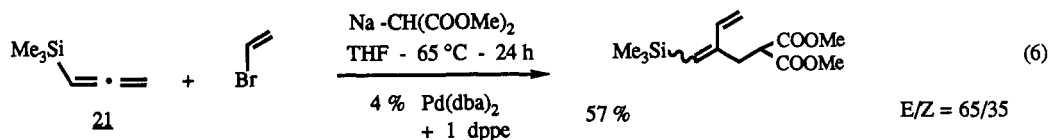
The enantioselective access to these  $\alpha$ -amino acids **20** was formally possible if a chiral phosphine ligand was associated to the catalytic system; but the relatively high temperature ( $55-60^\circ\text{C}$ ) of the reaction excluded this possibility, which has been successfully observed in the allylic series at low temperature (ref. 16).

## III SYNTHESIS AND APPLICATIONS OF DIENYLSILANES

Dienylsilanes of synthetic utility may be gathered in four classes I-IV (scheme 7). These compounds should present, beside the common properties of their dienic system, the specific reactivities of vinylsilanes (class I and II) or allylsilanes (classes III and IV) which have been previously demonstrated and used as synthetic tools (ref. 17). With the aim to find an easy access to functionalized dienylsilanes, we imagine their preparation via two carbometallation processes, the carbopalladation of silylated allenes **21** and **22** or the carbopalladation of an allenic hydrocarbon by a silylated vinylic species derived from **23** (scheme 8).



Reaction of trimethylsilyllallene **21** with vinylbromide and dimethyl sodiomalonate according to our standard procedure effectively produced a silylated malonate in a 57 % yield (eq. 6) (ref. 18).



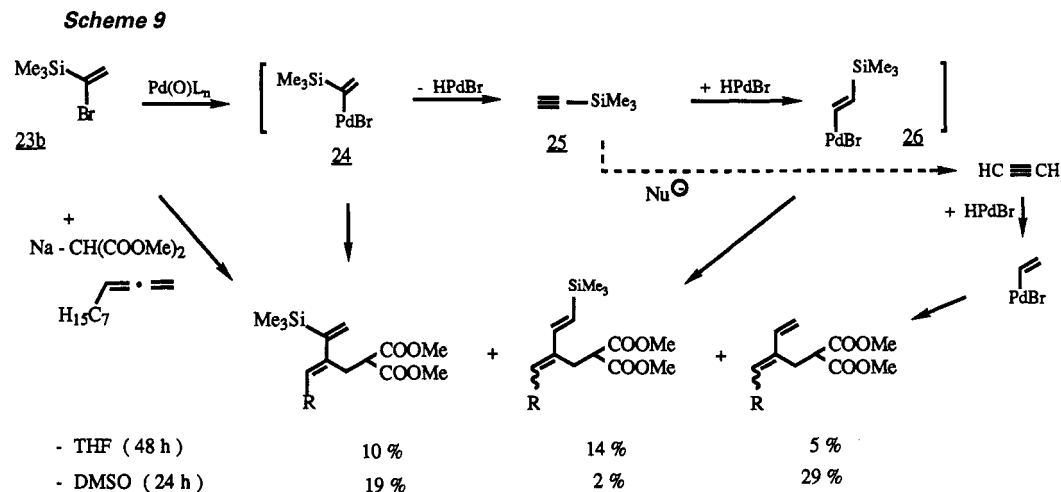
(Trimethylsilyl)methylallene **22** reacted as well with vinyl and isopropenyl bromide (eq. 7); but lower yields were obtained presumably because of the competitive decomposition of the allene **22** and/or the silylated intermediate  $\pi$ -allyl complex (ref. 18).

The alternative methodology using silylated vinylic bromides **23** was then tested and seemed more general for the success of our aim. Results of the palladium-catalyzed reactions of these bromides with allene or 1,2-decadiene and different malonate type anions are given in Table 4 (ref. 19).

TABLE 4. Synthesis of functionalized silylated dienic compounds .

Allene <i>I</i>	vinyl derivative <b>23</b>	Nucleophile	isolated yield
$\text{H}_2\text{C}=\text{C}=\text{CH}_2$		$\begin{matrix} < \text{Z} \\ < \text{Z} \end{matrix}$ (Z = COOMe)	 75 %
$\text{H}_{15}\text{C}_7$	"	"	 E/Z = 60/40 50 %
$\text{H}_2\text{C}=\text{C}=\text{CH}_2$		"	 40 %  24 %
$\text{H}_2\text{C}=\text{C}=\text{CH}_2$		"	 65 %
"	"	$\begin{matrix} < \text{CO-Me} \\ < \text{COOMe} \end{matrix}$	 89 %
"	"	$\begin{matrix} < \text{CO-Me} \\ < \text{COOMe} \\ \text{Me} \end{matrix}$	 85 %

Bromides **23a** and **23c** gave the expected diensilanes of classes I and IV with fairly good yields (50-90 %), whereas bromide **23b** led to more complex reaction products, with the formation of two silylated dienes and a desilylated diene; the formation of the unexpected diene is due to the rearrangement of the intermediate  $\sigma$ -vinylic palladium complex **24** which is explained in scheme 9.



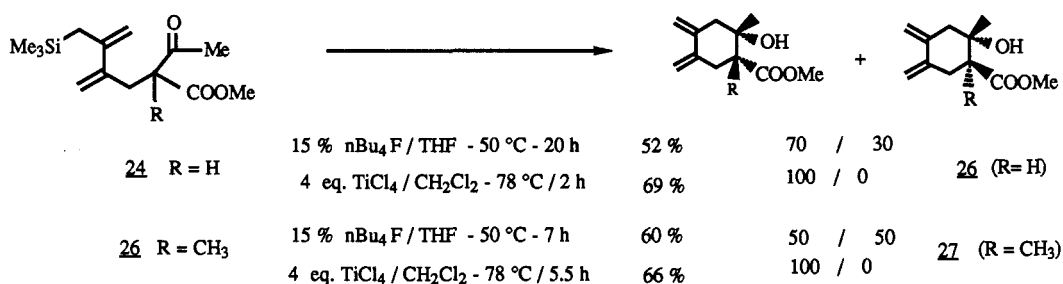


This rearrangement to the more stable complex **26**, which might proceed through  $\beta$ -elimination of HPdBr followed by its reverse addition to trimethylsilylacetylen **25**, would be the consequence of steric hindrance around the  $\sigma$ -vinyl C-Pd bond. Desilylation occurred more likely via acetylen from the assumed intermediate silane **25**.

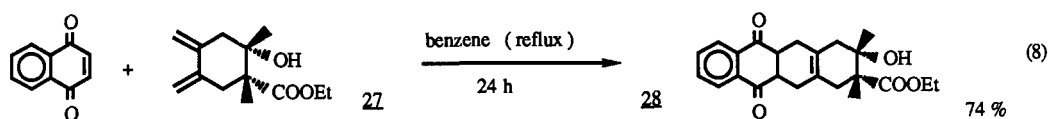
### Synthesis of 1,2-dimethylenecyclohexanes

The functionalized dienylsilanes of class IV, obtained from bromide **23c**, are valuable substrates for they may lead to 1,2-dimethylenecyclohexanes through Lewis acid induced cyclization or fluorine anion catalysis. Scheme 10 summarized the result obtained from acetylacetates **24** and **26**. Cyclisations with TiCl<sub>4</sub> afforded diastereoselectively the cis dienic hydroxyesters **26** and **27**; this selectivity might be the consequence of a tight chelation of the Lewis acid by the two carbonyl groups of the acetoacetates.

Scheme 10

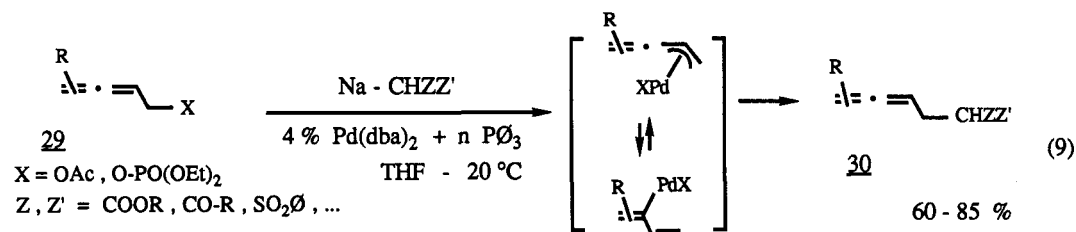


An example of application of this access to 1,2 dimethylcyclohexanes is given by the Diels-Alder reaction of cis-**27** with naphthoquinone: this cycloaddition affords the tetracyclic compound **28** which presents some of the basic functionalities of the anthracyclinone family (eq. 8).



### IV APPLICATION TO CARBOCYCLISATION

The cyclisation of an internal nucleophile with a  $\pi$ -allyl complex is known (ref. 20). Thus, an intramolecular version of our carbopalladation process could be easily designed starting from suitable substrates which include both the allenic pattern and a potential nucleophilic pole. Such substrates, namely  $\gamma$ -allenic diesters **29**, which had been previously obtained in our laboratory by the palladium-catalyzed substitution of the esters **29** of  $\alpha$ -allenic alcohols with delocalized anion (eq. 9) (ref. 21) offered this possibility.



The assumed intermediate  $\pi$ -allyl complexes **31** resulting from the carbopalladation step of these allenic diesters **30** should lead to vinylcyclopropanes or vinylcyclopentenes, according to the cyclisation center of these intermediates with the internal nucleophile (scheme 11). Regioselectivity of the ring closure was found to be dependent on both the steric hindrance of the vinylic component and the substitution of the allenic diester **30**.

Table 5 shows the results of the cyclization reactions of compounds **30a-c** with several vinylic bromides: all the diesters led with a high regioselectivity to vinylcyclopentenes **32** (run 2-7), except diester **30a** with vinylbromide which afforded a vinylcyclopropane diester **33** as a sole product (run 1).

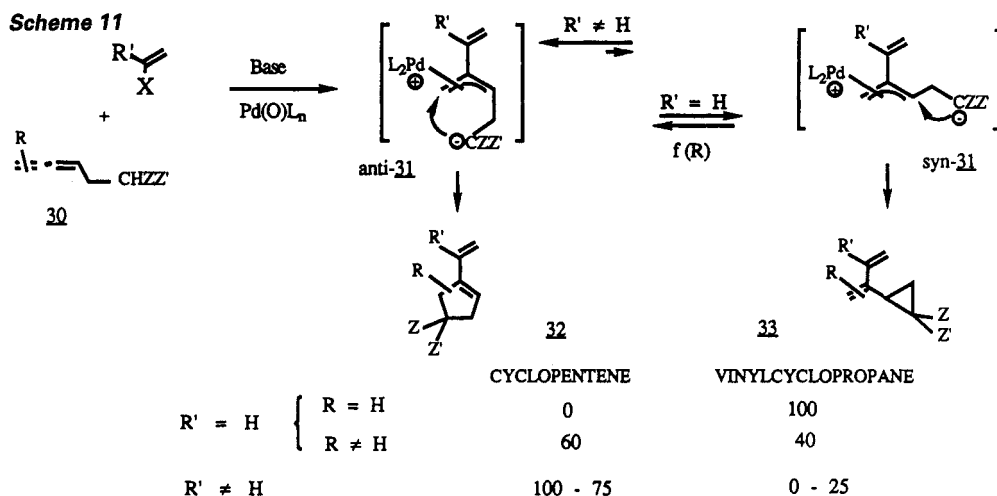
A likely mechanistic rationalization for the observed ring closure pathways, lies on the relative stability of the two possible anti and syn configurations of the intermediate complex **31**. The anti-**31** configuration would lead to the five-membered ring cyclisation. Isomerisation to the syn-**31** configuration would be favoured when the vinylic bromide is unhindered ( $R'=H$ ); this last intermediate then cyclizes to a vinylcyclopropane **33** (run 1).

Thus, intermediates **31** which have an unsaturated group on their central carbon atom, present a high propensity to give vinylcyclopentenes (ref. 22) unlike unsubstituted ones which always lead to vinylcyclopropanes (ref. 23). This emphasizes the synthetic utility of this ring closure procedure; particularly, vinyl cyclopentenic substrates **32** should be valuable dienic intermediates for the synthesis of polycyclic molecules via cycloaddition.

TABLE 5. Palladium-promoted carbocyclisation of  $\gamma$ -allenic diesters **30**.

Run	$\text{R} \cdot \text{C}=\text{C}=\text{C}-\text{CHZZ}$ <b>30</b>	$\text{R}'-\text{C}=\text{C}-\text{X}$ vinyl derivative	THF 4% Pd(dba) <sub>2</sub> + dppe cyclisation conditions	$\text{R}'-\text{C}=\text{C}-\text{C}(\text{Z})_2-\text{C}(\text{Z})=\text{C}$ <b>32</b>	$\text{R}'-\text{C}=\text{C}-\text{C}(\text{Z})_2-\text{C}(\text{Z})_2$ <b>33</b>	isolated yield
1	$\text{CH}_2=\text{C}(\text{R})-\text{C}(\text{R}')=\text{C}-\text{CHZZ}$ <b>30a</b>	$\text{CH}_2=\text{C}(\text{R}')-\text{Br}$	65 °C / 15 h			80 %
2	"	$\text{CH}_2=\text{C}(\text{R}')-\text{Br}$	40 °C / 16 h	$\text{R}'-\text{C}(\text{Z})_2-\text{C}(\text{Z})=\text{C}$ 75 / 25		71 %
3	"	$\text{C}_6\text{H}_5-\text{C}(\text{R}')=\text{C}-\text{Br}$	65 °C / 12 h	$\text{R}'-\text{C}(\text{Z})_2-\text{C}(\text{Z})=\text{C}$ 96 / 4		50 %
4	"	$\text{C}_6\text{H}_5-\text{C}(\text{R}')=\text{C}-\text{I}$	65 °C / 5 h	$\text{R}'-\text{C}(\text{Z})_2-\text{C}(\text{Z})=\text{C}$		65 %
5	$\text{CH}_2=\text{C}(\text{R})-\text{C}(\text{R}')=\text{C}-\text{CHZZ}$ <b>30b</b>	$\text{CH}_2=\text{C}(\text{R}')-\text{Br}$	65 °C / 4 h	$\text{R}'-\text{C}(\text{Z})_2-\text{C}(\text{Z})=\text{C}$ 68 / 32		60 %
6	"	$\text{CH}_2=\text{C}(\text{R}')-\text{Br}$	40 °C / 6 h	$\text{R}'-\text{C}(\text{Z})_2-\text{C}(\text{Z})=\text{C}$		72 %
7	$\text{CH}_2=\text{C}(\text{R})-\text{C}(\text{R}')=\text{C}-\text{CHZZ}$ <b>30c</b>	$\text{CH}_2=\text{C}(\text{R}')-\text{Br}$	40 °C / 5 h	$\text{R}'-\text{C}(\text{Z})_2-\text{C}(\text{Z})=\text{C}$		57 %

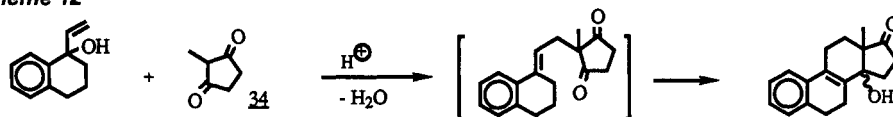
Scheme 11



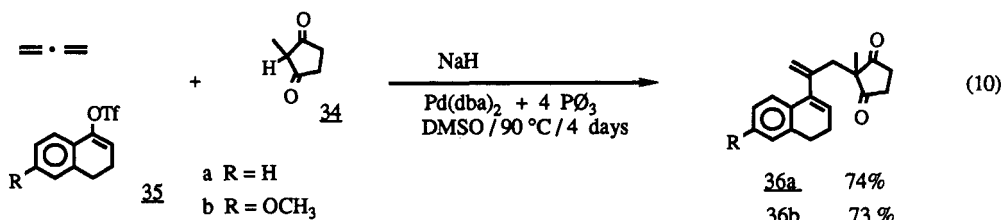
## V STEROIDS SYNTHESIS

Methyl 1,3-cyclopentadiene **34** has been largely employed as a precursor of the D ring of steroids, particularly in the so-called Torgov reaction (scheme 12) (ref. 24).

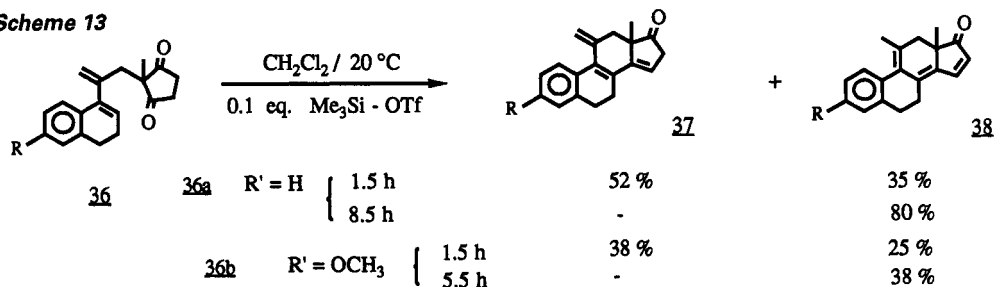
Scheme 12



We have used this dione **34** as the anion precursor of our dienes synthesis. Associated with bicyclic enol triflates **35** and allene, it led to dienic substrates **36** which already present the preformed A, B, D ring system of steroids (eq. 10).



Scheme 13



The cyclisations of these last substrates **36** were carried out with several acidic agents (HClO<sub>4</sub>, pTSA, CF<sub>3</sub>SO<sub>3</sub>H, Me<sub>3</sub>Si-OTf). Trimethylsilyltriflate Me<sub>3</sub>Si-OTf appeared as the milder one (scheme 13); two trienic keto steroids **37** and **38** were then obtained according to the reaction conditions (ref. 25).

Thus, these last reactions allow a short two step route to 11-substituted derivatives of important steroid compounds, since ketones **36** can be transformed to 11-methyl-19-nor steroids (26).

## CONCLUSION

This work has pointed out that the carbopalladation of allenes, allows the easy formation of unsaturated  $\pi$ -allyl palladium complexes. This process followed by the reaction of an appropriate carbonucleophile, sets up a straightforward regio and stereoselective synthesis of functionalized dienic compounds. The synthetic use of these last unsaturated substrates in the elaboration of more complex molecules emphasizes the utility of allenes as valuable synthetic building blocks.

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