Strain, silyl and steric effects on the regioselectivity of palladium(0) catalyzed allyl esters reduction as alternative to the Wittig reaction

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Abstract

1-(1-alkenyl)- (**1a–g**) and 1-(1-cycloalkenyl)cycloalkyl esters (acetate, tosylate, mesylate) (**4a–d**) underwent palladium(0) catalyzed hydrogenolysis by sodium formate or *n*-butylzinc chloride as hydride sources. The regioselectivity of the reduction can be monitored either by ring strain, silyl substitution of the allyl moieties or by using the steric effect of trivalent phosphorus ligands related to their cone angles θ. Alkylidenecycloalkanes (**2a–g**) and cycloalkylidenecycloalkanes (**5a–d**) have been obtained, generally in good yields, thus providing a convenient alternative to the Wittig olefination and a new access to allylsilanes.

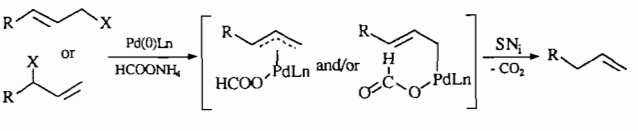
Key words: Catalysis; Reductive cleavage; Palladium complexes; Allyl complexes; Steric effects

Palladium(0) catalyzed reductive cleavage of allylic compounds such as formates, acetates, carbonates, chlorides, sulfonates, aryl and aliphatic ethers, vinyl epoxydes, sulfides, sulfones, selenides, silyl ethers, ... provided convenient synthetic means for the regioselective preparation of terminal alkenes [1, 2] or 2-alkenes [3]. The regiochemistry was not only dependent on steric and electronic factors [4] but also on the nature of the hydride sources. Thus, hydrogenolysis of allylic acetates and phenyl ethers with ammonium formate (or formic acid–triethylamine) using a palladium(0)–phosphine complex as catalyst provided 1-olefins, predominantly; 0–30% of 2-olefins, depending strongly on the structures of the allylic compounds and phosphine ligands, were formed as by-products [2].

π-Allyl palladium formate complexes, recently characterized by ^{1}H and ^{13}C NMR spectroscopy [5], and/or σ-allyl palladium complexes [2] were considered as key intermediates, which then underwent either decarboxylation of the formate ligand and attack of the hydride on the more substituted end of the allylic systems [4] or SNi transfer of hydride from formate complexed to the preferred terminal σ-Pd species [2, 6]. Allylic formates have also been used for the same intramolecular transformation, in this case use of ammonium formate as external hydride source was not necessary [2a, d], (Scheme 1).

On the other hand, the palladium(0) catalyzed reaction of allyl acetates with alkylzinc derivatives containing β-hydrogens as hydride sources (β-elimination) took a different reaction path. For instance reaction of the *E* geranyl acetate (R = 4-methyl pent-3-enyl) with n-butylzinc chloride in the presence of $Pd(PPh_3)_4$ (5 mol%) gave a 94:6 mixture of *E*- and *Z*-2,6-dimethyl-2,6-octadienes (96% yield), besides 3% of the corresponding 1-olefins. Analogously, the *Z* isomer, i.e. neryl acetate, led to these 2-olefins under the same conditions, but with the reverse geometrical selectivity (ratio *E*/*Z*: 6/94) [3].

The intermediacy of σ-allylbutyl palladium complexes was considered to explain the regioselectivity and ste-



X=OAc, OCO_2CH_3, OPh

Scheme 1.

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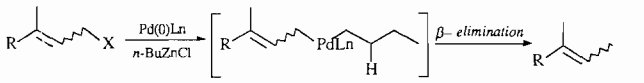


X = OAc, Cl, OTs

R = $(CH_3)_2$ C=C-CH_2CH_2

Scheme 2.

reospecificity of this hydrogenolysis by attack of the hydride arising from β-elimination, on the less substituted site of the π-allyl palladium complexes [3] (Scheme 2).

Other hydride transfer reagents were effective. Very potent nucleophilic hydride sources (e.g. $LiAlH_4$, $LiBHEt_3$) rapidly attacked the intermediate π-allyl complexes at the less hindered terminal site to provide 2-olefins; while less effective hydride transfer reagents (e.g. $NaBH_3CN$, $NaBH_4$) may attack preferentially the π-allyl systems at the site best able to accommodate positive charge for instance by inductive effect, leading to 1-olefins [4].

We have investigated and report herein the effects of ring strain [7], silyl substitution and steric hindrance of the phosphorus ligands on the regioselectivity of the palladium(0) catalyzed reduction of allyl esters, e.g. 1-(1-alkenyl) and 1-(1-cycloalkenyl)cycloalkane esters in order to determine the scope and limitation of this hydrogenolysis with the aim of providing a convenient alternative to the Wittig reaction, especially to prepare readily three- or tetrasubstituted olefins [8].

As shown in Table 1, reaction of 1-acetoxy-1-ethenylcyclohexane (**1a**) [9] ($n=4$, R=H, X=OAc) with sodium formate (3 equiv.) and [15]-crown-5-ether (10%) as hydride source in THF, in the presence of bis(dibenzylideneacetone)palladium [$Pb(dba)_2$] and triphenylphosphine (PPh_3) (ratio 1:2) [8, 10] gave in 87% yield a 13:31:56 mixture of ethylidenecyclohexane (**2a**) [11], ethenylcyclohexane (**3a**) [12] and 1-ethenylcyclohexene* arising from elimination of one equivalent of AcOH [14], (entry 1). In the meantime, it has been reported that treatments of 1-vinylcyclohexyl methyl carbonates, for instance 4-t-butyl-1-ethenylcyclohexyl methyl carbonate, with formic acid and triethylamine in the presence of palladium bis(acetylacetonate) [$Pd(acac)_2$] and tri-n-butylphosphine $P(n\text{-}Bu)_3$ led to 1-ethenylcyclohexene, exclusively (entry 2) [15]. On the other hand, reaction of **1a** with 4 equiv. of n-butylzinc chloride (from n-BuLi and $ZnCl_2$), in the presence of $Pd(dba)_2/PPh_3$ (ratio 1:2) provided a 99:1 mixture of ethylidenecyclohexane (**2a**) [11] and ethenylcyclohexane (**3a**) [12], (entry 3); thus offering a convenient alternative to the Wittig reaction of the strongly basic cyclohexylidenetriphenylphosphorane, which is known to induce enolate formation of ketones rather than the expected olefination [16].

Reaction of *E*-1-acetoxy-1-(2-trimethylsilylethenyl)-cyclohexane (**1b**) ($n=4$, R=$SiMe_3$, X=OAc), prepared by acetylation (Ac_2O, DMAP) of 1-(trimethylsilylethenyl)cyclohexanol [17], in THF or acetonitrile at room temperature with sodium formate in the presence of [15]-crown-5 ether (10%) as hydride source and with 5% of $Pd(OAc)_2/PPh_3$ (ratio 1:2) as catalyst gave in 89% yield a 89:11 mixture of 1-(trimethylsilylethylidene)cyclohexane (**2b**) [18] and (2-trimethylsilylethenyl)cyclohexane (**3b**) [19]; both hydrogenolysis products were readily identified from the ^1H NMR spectra of the crude mixture (entry 4). Likewise reaction of **1b** with n-BuZnCl (4 equiv.) in the presence of $Pd(OAc)_2/PPh_3$ led in 87% yield to an analogous 88:12 mixture of the regioisomers **2b** and **3b** (entry 5).

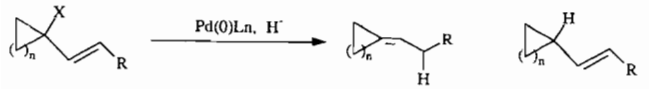
E-1-Acetoxy-1-(2-triethylsilylethenyl)cyclohexane (**1c**) ($n=4$, R=$SiEt_3$, X=OAc), prepared by hexachloroplatinic acid (H_2PtCl_6) catalyzed hydrosilylation of commercially available 1-ethynylcyclohexanol by triethylsilyl hydride (Et_3SiH) [20], followed by acetylation, underwent reaction with sodium formate and [15]-crown-5 ether (10%) as hydride source, and with 5% of $Pd(OAc)_2/PPh_3$ (ratio 1:2) as catalyst to lead to a 96:4 mixture of (2-triethylsilylethylidene)cyclohexane (**2c**) [21] and (2-triethylsilylethenyl)cyclohexane (**3c**) [22], readily identified from the ^1H NMR spectra of the crude mixture (entry 6). Otherwise, reaction of **1c** with n-BuZnCl in the presence of $Pd(dba)_2/2PPh_3$ as catalyst, led in 81% yield to a 63:37 mixture of the regioisomers **2c** and **3c** (entry 7).

This palladium(0) catalyzed hydride reduction of 3-(trialkylsilyl)allyl acetates offered therefore a convenient alternative to the preparation of allylsilanes from the reaction of allyl acetates with silylcuprates reagents such as $[C_6H_5Si(CH_2)_2]_2CuLi$ [23], from the reaction of allyl phosphates with (dimethylphenylsilyl)-diethylaluminum [24] or from the palladium(0) and molybdenum(0) catalyzed substitution of allyl acetates by tris(trimethylsilyl)aluminum which was reported to occur with a regioselectivity highly sensitive to the reaction conditions [25].

Exclusively formation of vinylsilanes has been reported to occur from the palladium(0) catalyzed substitution of trimethylsilylallyl acetates by stabilized (soft) nucleophiles, such as enolates of malonic esters, β-dicarbonyl compounds, β-sulfonyl esters or enamines [26, 27] and from the reaction of trimethyl substituted allylic iron cations with silyl enol ethers, silyl ketene acetals and allyltin [28]. As far as we know, only one example of palladium(0) catalyzed hydrogenolysis of silyl-substituted allyl carbonate by formate has been reported to provide an allylsilane.

*For the conversion of allylic acetates into conjugated dienes under the influence of palladium complexes, see ref. 13.

TABLE 1. Palladium(0) catalyzed reduction products of 1-(1-alkenyl)cycloalkyl esters (**1a–1g**)



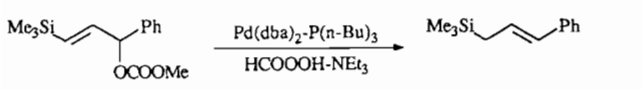
1a n=4, R=H; **b** SiMe$_3$; **c** SiEt$_3$; **d** C$_4$H$_9$; **e** n=1, R= C$_4$H$_9$; **f** SiMe$_3$; **g** C$_6$H$_5$

Entry	*n*	R	X	H	Ln	*y* (%)	Ratio
1	4	H	OAc	HCOONa[a]	PPh_3	87	13:31[a]
2			OCO_2Me	HCOOH, NEt_3	PBu_3	80	0:100[c]
3			OAc	n-BuZnCl	PPh_3	83	99:1
4		$SiMe_3$	OAc	HCOONa[a]	PPh_3	89	89:11
5				n-BuZnCl	PPh_3	87	88:12
6		$SiEt_3$	OAc	HCOONa[a]	PPh_3	86	96:4
7				n-BuZnCl	PPh_3	81	63:37
8		C_4H_9	OAc	HCOONa[a]	PPh_3	85	42:58
9					P(mesityl)$_3$	40	59:41
10				HCOONa[a]	dppf[d]	85	38:62
11				HCOOH, NEt_3	PBu_3	84	38:62
12				n-BuZnCl	PPh_3	79	61:39
13	1	C_4H_9	OTs	HCOONa[a]	dppe	81	50:50
14					PPh_3	80	100:0
15				n-BuZnCl	PPh_3	85	0:100
16		$SiMe_3$	OTs	HCOONa[a]	PPh_3	90	100:0
17				n-BuZnCl	PPh_3	85	0:100
18		Ph	OTs	HCOONa[a]	dppe	90	37:63
19					PPh_3	95	62:38
20				n-BuZnCl	PPh_3	93	0:100
21					P(mesityl)$_3$	75	16:84

[a]Hydrogenolysis by sodium formate was performed in the presence of 10 mol% of [15]-crown-5 ether in order to improve the yield, see refs. 8 and 10. [b]1-Vinylcyclohexene was formed as major by-product (56%). [c]From ref. 15. [d]dppf: bis(diphenylphosphino)ferrocene.

Thus, when methyl 1-phenyl-3-trimethylsilylallyl carbonate was treated with a 1:1 mixture of formic acid and triethylamine in the presence of the palladium catalyst ($Pd_2(dba)_3$, $CHCl_3$, PBu_3) in THF at reflux, 1-phenyl-3-trimethylsilylpropene was obtained in 58% yield, as major product (81% pure as monitored by GLC) (Scheme 3) [29].

Comparison of the hydrogenolysis products reported in Table 1, suggests the likely occurrence of the σ-3,3-(pentamethylene)allyl palladium complexes **A** (R=H) (100%) [2] and **B** (R=H) (99%) [3], where the palladium could be positioned on the least substituted allylic carbon, as intermediates in the reductions of **1a** by formate ammonium (entry 2) and n-butylzinc chloride (entry 3), respectively; while, hydrogenolysis of **1b,c** would suggest the intermediacy of the σ-1,1-(pentamethylene)allyl palladium complex **C** (R = $SiMe_3$, $SiEt_3$)

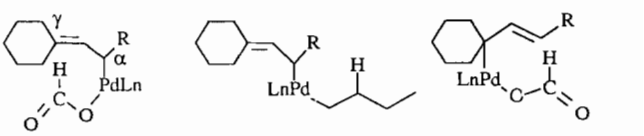


58% (81% pure g.c.)

Scheme 3.

(89–96%) [2], with the palladium in the γ position of the trialkylsilyl group when formate was used as hydride source (entries 4, 6), and the major intermediacy of the σ-3,3-(pentamethylene)allyl palladium complex **B** (R = $SiMe_3$, $SiEt_3$) (63–88%) with n-butylzinc chloride (entries 5, 7) [3], now with the palladium in the α position of the silyl group (Scheme 4).

Frontier orbital control has been reported to direct attacking nucleophiles on the η^3-allyl group [30]. The trialkylsilyl group was considered to polarize the frontier orbitals of the system on the γ-carbon, thus stabilized (soft) nucleophiles which should react with the carbon having the largest coefficient in the LUMO added to



A R=H (100%); C_4H_9 (69%)

B R = H (99%); C_4H_9 (61%); $SiMe_3$ (88%); $SiEt_3$ (63%)

C R = $SiMe_3$ (89%); $SiEt_3$ (96%)

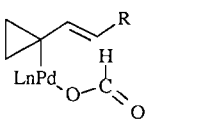
Scheme 4.

the γ-carbon providing vinylsilanes, exclusively. On the other hand, with non-stabilized (hard) nucleophiles which attacked directly the palladium (transmetallation) it appeared clearly that the Pd–Nu fragment was displaced either towards the γ-carbon center (σ-palladium complex **C** with formate), considered to have the largest coefficient in the HOMO and therefore able to provide the best σ-bonding of palladium, or to the α-carbon center (σ-palladium complex **B** with n-butylzinc chloride) in order to provide allylsilanes, preferentially, whatever the hydride source. Although β-silyl groups were reported to reduce the electrophilicity of α,β-enones [31a, c], these hydride reductions of allylic acetates **1b, c** bearing a trialkylsilyl substituent led to allylsilanes which can then undergo further electrophilic substitutions [32]. Moreover, protodesilylation by fairly weak acids or Lewis acids occurred with double bond migration giving in these cases, ethenylcyclohexanes from **2b,c**, while nucleophilic desilylation by alkoxides or fluoride anions usually led to the more-substituted alkenes regardless of the site of the silyl group; therefore these methods can appear complementary [33].

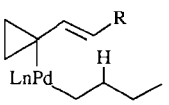
Hydrogenolysis of *E*-1-acetoxy-1-(1-hexenyl)cyclohexyl acetate (**1d**) ($n=4$, $R=C_4H_9$, $X=OAc$), obtained by successive reduction ($LiAlH_4$) and acetylation of 1-(1-hexynyl)cyclohexanol [34], by the reductive system HCOONa, [15]-crown-5 ether in the presence of $Pd(dba)_2$–$2PPh_3$ as catalyst, gave in 85% yield a 42:58 mixture of hexylidenecyclohexane (**2d**) [9b] and *E*-(1-hexenyl)cyclohexane (**3d**), identified from the ^1H NMR spectra of the crude mixture (entry 8). Use of trimesitylphosphine [P(2,4,6-trimethylphenyl)$_3$] as bulky palladium ligand [35], favored only slightly the formation of the cyclohexylidene **2d** (59%) (entry 9). On the other hand, bis(diphenylphosphino)ferrocene (dppf) as palladium ligand favored the formation of the vinylcyclohexane **3d** (62%) (entry 10). Likewise the $HCOOH$–NEt_3, $Pd(dba)_2/PBu_3$ reductive system [2], which is known to induce substitution by hydride at the more substituted site of π-allyl palladium complexes [2c], led also preferentially to **3d** (62%), besides the hexylidene **2d** (38%) (entry 11). As expected, reverse regioselectivity was observed with n-BuZnCl as hydride source [3], which under palladium(0) catalysis preferentially reduces the acetate **1d** into the hexylidene **2d** (61%) (entry 12); in these cases intermediate formation of σ-complexes **A** ($R=C_4H_9$) (62%) and **B** ($R=C_4H_9$) (61%) were also favored but to a smaller extent (Scheme 4).

Ethenylcyclopropyl acetates underwent palladium(0) catalyzed nucleophilic substitution with low reactivity, comparatively to current allylic acetates, but better leaving groups, i.e. tosylate or mesylate have been reported to increase dramatically the reactivity of these allyl esters with however the same regioselectivity [10]. Thus hydrogenolysis of *E*-1-(1-hexenyl)-1-tosyloxycyclopropane (**1e**) ($n=1$, $R=C_4H_9$, $X=OTs$), prepared by successive reduction and esterification (*p*-toluenesulfonyl chloride, pyridine or triethylamine) of 1-(1-hexynyl)cyclopropanol readily available from cyclopropanone hemiacetal [36, 37], with sodium formate and [15]-crown-5 ether in the presence of 5% of palladium(0)-bis(diphenylphosphino)ethane [$(Pd(dba)_2$-dppe)] led in 81% yield to a 50:50 mixture of hexylidenecyclopropane (**2e**) [38] and *E*-(1-hexenyl)cyclopropane (**3e**) (entry 13). But hydrogenolysis of the sulfonate **1e** with HCOONa-[15]-crown-5 ether in the presence of $Pd(dba)_2$ and PPh_3 (ratio 1:2) induced in 80% yield, exclusive formation of the cyclopropylidene **2e** [38] (entry 14); while hydrogenolysis of **1e** with n-butylzinc chloride as hydride source in the presence of $Pd(dba)_2/2PPh_3$ yielded the cyclopropane **3e** (85%), exclusively (entry 15).

Unsymmetric π-allyl palladium complexes with the palladium positioned closer to the allylic carbon bearing the least pronounced positive charge [10, 39] or σ-allyl complexes with the palladium occupying the least substituted allylic carbon [40, 41] have been considered as intermediates to take into account the regioselectivity of the palladium catalyzed nucleophilic allylic substitutions and several NMR data [41, 42]. Effectively, when primary versus tertiary substitution were competiting like in **1a**, hydrogenolysis products arising from σ-complexes **A** or **B** (R = H), were obtained, selectively (99–100%) (Table 1, entries 2 and 3). But, from **1d** where secondary versus tertiary substitutions were competiting, difference of charge density and therefore regioselectivity were somewhat lower (61–62%), entries 8–12. However this regioselectivity can be dramatically enhanced and oriented by strain effect; thus comparison of entries 8 with 14 and 12 with 15, showed that the intermediate allyl palladium complexes formed from the cyclopropyltosylate **1e** were really unsymmetric with the palladium positioned on the cyclopropyl carbon where the positive charge should be less pronounced (strained cyclopropyl cation highly defavored by strain effect) [43], so entailing formation of the σ-1,1-(dimethylene)allyl palladium complexes **D** ($R=C_4H_9$) and **E** ($R=C_4H_9$) as exclusive intermediates (100%) [10] (Scheme 5).



D R = C_4H_9 (100%)
$SiMe_3$ (100%)



E R = C_4H_9 (100%)
$SiMe_3$ (100%)

Scheme 5.

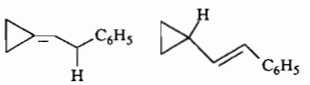
Hydrogenolysis of *E*-1-tosyloxy-1(2-trimethylsilylethenyl)cyclopropane (**1f**) [44], prepared by reduction ($LiAlH_4$) and esterification (tosyl chloride, NEt_3, DMAP) of 1-(trimethylsilylethynyl)cyclopropanol readily available from the cyclopropanone hemiacetal [36, 37], with sodium formate and [15]-crown-5 ether in the presence of 5% of palladium(0) [$Pd(dba)_2$-$2PPh_3$], gave in 90% yield, exclusively the (2-trimethylsilylethylidene)cyclopropane (**2f**) (entry 16); while reaction with n-butylzinc chloride in the presence of Pd(0) [$Pd(dba)_2$-$2PPh_3$], led in 85% yield, to the *E*-(2-trimethylsilylethenyl)cyclopropane (**3f**), exclusively, as evidenced from the NMR spectra of the crude products (entry 17). Therefore in these cases, both strain and silyl effects direct exclusive formation of the σ-1,1-(dimethylene)allylpalladium complexes **D** ($R = SiMe_3$) and **E** ($R = SiMe_3$) (Scheme 5).

The *E*-1-(1-styryl)-1-tosyloxycyclopropane (**1g**) ($n = 1$, $R = C_6H_5$, X = OTs), also readily available as **1f**, from the cyclopropanone hemiacetal [10, 36, 37], underwent hydrogenolysis by sodium formate and 10 mol% of [15]-crown-5 ether in the presence of $Pd(dba)_2$ and dppe to give in 90% yield a 37:63 mixture of (2-phenylethylidene)cyclopropane (**2g**) and *E*-styrylcyclopropane (**3g**) [45] (entry 18). Use of triphenylphosphine (PPh_3) as ligand of the palladium catalyst favored only slightly formation of the methylenecyclopropane **2g** (ratio **2g**:**3g** = 62:38) (entry 19) when compared with the hydrogenolysis products ratio of **1e** (entry 14) because conjugation effect appeared to favor formation of styryl compound **3g** and therefore limited the directive effect of strain. As expected, palladium(0) catalyzed hydrogenolysis of **1g** with n-BuZnCl as hydride source [3], gave in 93% yield the vinylcyclopropane **3g**, exclusively, when using PPh_3 as palladium phosphine ligand (entry 20). While use of trimesitylphosphine appeared to induce by steric hindrance formation of 16% of methylenecyclopropane **2g** (entry 21).

Steric effect of trivalent phosphorus ligands can dominate the chemical behavior of transition metal complexes [46]. The steric parameter for symmetric ligands is the apex angle θ of a cylindrical cone centered 2.28 Å from the center of the phosphorus atom, which touches the van der Waals radii of the outermost atoms of the ligands [35]. These angles have been correlated with a wide variety of phenomena including stabilities [47], fluxional behaviour [48], rate constants [49], catalytic activities [50], specificities in product formation [50]. Correlation has been established between proton NMR shifts and the cone angles providing convenient means for determining the size of phosphorus ligands [15]; combinations of steric and electronic factors have been pointed out to explain the ligand effect on the formation of products resulting from rhodium catalyzed hydroformylation of conjugated dienes [52]. The dominance of steric factors has been observed in the control of isomeric distribution in the cyclooligomerization of butadiene on nickel–phosphorus ligand catalysts [53]. Recently, the regioselective α-arylation of acyclic enol ethers by aryl halides and trifluoromethanesulfonates (Heck reaction) has been proved to be dependent of the relationship between the phosphine ligands and counterions (leaving groups); the α-regioselectivity seemed to increase with the coordinating ability of phosphines to palladium, in correlation with the cone angle θ [54].

As shown in Table 2, the regioselectivity of the palladium(0) catalyzed hydrogenolysis of *E*-1-(1-styryl)-1-tosyloxycyclopropane (**1g**) [10] by sodium formate and [15]-crown-5 ether, appeared also greatly affected by the nature of the ligands. An increase of the size of the substituents on phosphorus will increase the cone angle θ and the bond lengths of metal to phosphines, so decreasing their coordinating ability (reduction of the s character in the phosphorus lone pair) and favoring coordination of other competitive ligands for instance the π-allyl moiety [35]; effectively, varying θ from 145° (PPh_3) to 194° ($P(o\text{-anisyl})_3$) [35, 52, 55] appeared to favor the formation of the methylenecyclopropane derivative **2g** [10], from 62 to 90%, although more strained than **3g** (*SE*(methylenecyclopropane) − *SE*(cyclopropane) = 13.4 kcal/mol [56]) and not conjugated (Table 2, entries 2, 3, 5 and 6). In fact, it has been reported from IR data (comparison of the C=O stretching frequencies of tetracarbonyl iron complexes) that methylenecyclopropanes form more stable π-olefin

TABLE 2. Relationship between the cone angle θ of phosphine ligands and the regioselectivity of palladium(0) catalyzed hydrogenolysis of 1-(1-alkenyl)cyclopropyl sulfonates (**1g**) by sodium formate



2 g 3 g

Entry	Ln	θ (°)	y (%)	Ratio
1	dppe	125[a]	90	37:63
2	PPh_3	145[a]	95	62:38
3	$P(p\text{-anisyl})_3$	145[b]	90	78:22
4	$P(\alpha\text{-naphthyl})_3$	160[b]	45	0:100
5	$P(o\text{-tolyl})_3$	194[a]	94	85:15
6	$P(o\text{-anisyl})_3$	194[c]	90	90:10
7	$P(\text{mesityl})_3$	212[a]	19	0:100
8	dppf[d]		80	20:80

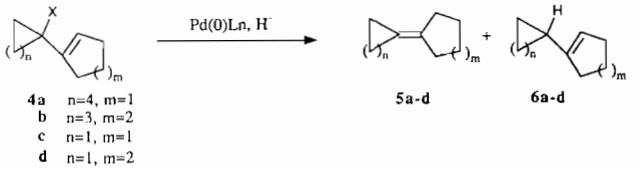
[a]From ref. 35. [b]From ref. 52. [c]From ref. 55. [d]Molecular structure of dppf has been established; it has been shown that bond lengths and angles involving the phosphorus atoms compare well with the values observed in free triphenylphosphine, but the apex cone angle θ has not been measured [72].

transition metal complexes than ethenylcyclopropanes [57].

On the other hand, bidentate diphosphines such as dppe ($\theta = 125°$), which are more metal chelating [35], favored styrylcyclopropane **3g** (63%) (entry 1). However, too large an increase of the size of the phosphine ligands can hamper the reaction and shift the position of nucleophilic attack by steric hindrance [58]; thus with P(mesityl)$_3$ ($\theta = 212°$, one of the highest cone angle reported value [35]) as ligand of Pd(0), hydrogenolysis of **1g** by formate, on heating in THF at reflux for 48 h, gave in 19% yield only, exclusively **3g**, besides the starting sulfonate **1g**, as evidenced from the NMR spectrum of the crude product (entry 7). Likewise, as reported in Table 1 entry 21, use of n-BuZnCl and P(mesityl)$_3$ led to **2g**, therefore involving at least partially an unsymmetric complex with the palladium not positioned on the cyclopropyl ring. Surprising also were the results observed in the hydrogenolysis of **1g** in the presence of Pd(dba)$_2$-tri(α-naphthyl)phosphine ($\theta = 160°$), which in rather low yield (45%) led to **3g** exclusively (entry 4), and with bis(diphenylphosphino)ferrocene (dppf) as ligand (θ not determined) providing in 80% yield **3g** as major product (80%) (entry 8). Significant distortions of ligands to minimize interaction and provide less sterically demanding complexes [59], or competiting steric and electronic factors, could also control this regioselectivity. An electronic effect has been clearly observed by using P(*p*-methoxyphenyl)$_3$ ($\theta = 145°$) which induced major formation of **2g** (78%) as formate hydrogenolysis product (entry 3), comparatively to PPh$_3$ ($\theta = 145°$) which gave **2g** (62%) (entry 2); it could also explain the increased ratio of **2g** obtained by using P(*o*-anisyl)$_3$ (90%) comparatively to P(*o*-tolyl)$_3$ (85%), although both phosphine ligands have the same cone angle ($\theta = 194°$), (entries 5 and 6).

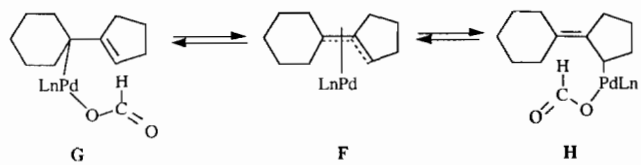
As shown in Table 3, treatment of 1-acetoxy-1-(1-cyclopentenyl)cyclohexane (**4a**) ($n = 4$, $m = 1$, X = OAc) [60] with HCOONa and [15]-crown-5-ether, in the presence of Pd(dba)$_2$ and 2PPh$_3$, provided in 88% yield a 26:74 mixture of cyclopentylidenecyclohexane (**5a**) [61] and (1-cyclopentenyl)cyclohexane (**6a**) [62] as evidenced from ^{1}H NMR spectra, coupled gas chromatography and mass spectrometry of the crude products (GC-MS) (entry 1). Tri(*o*-anisyl)phosphine or tri(α-naphthyl)phosphine as palladium ligand led also, with low regioselectivity, preferentially to **6a** (61–66%) involving hydride substitution at the more substituted site (entries 2, 3). Use of n-BuZnCl as hydride source provided a 52:48 mixture of tetra- and trisubstituted olefins **5a** and **6a**, whatever the palladium phosphine ligand, PPh$_3$ or P(*o*-anisyl)$_3$, i.e. whatever the cone angle values of 145 and 194°, respectively, *vide supra* (entries 4, 5). The results of these palladium(0) catalyzed

TABLE 3. Palladium catalyzed reduction products of 1-(1-cycloalkenyl)cycloalkyl esters (**4a–d**)



Entry	*n*	*m*	X	H$^-$	Ln	*y* (%)	Ratio
1	4	1	OAc	HCOONa[a]	PPh$_3$	86	26:74
2					P(*o*-anisyl)$_3$	81	34:66
3					P(naphthyl)$_3$	83	39:61
4				n-BuZnCl	PPh$_3$	79	52:48
5					P(*o*-anisyl)$_3$	81	52:48
6	3	2	OAc	HCOONa[a]	PPh$_3$	0[b]	
7				n-BuZnCl	PPh$_3$	0[b]	
8	1	1	OMs	HCOONa[a]	PPh$_3$	80	98:2
9				n-BuZnCl	PPh$_3$	83	0:100
10	1	2		HCOONa[a]	PPh$_3$	85	98:2

[a]Hydrogenolysis by sodium formate was performed in the presence of 10 mol% of [15]-crown-5 ether in order to improve the yield, see refs. 8 and 9. [b]1-(1-Cyclopentenyl)cyclohexene resulting from elimination of AcOH was formed as unique product.



Scheme 6.

reductions must be compared with the acid induced dehydration of 1-cyclohexylcyclopentanol by potassium hydrosulfate ($KHSO_4$) or zinc chloride ($ZnCl_2$) which provided 35:65 and 37:63 mixtures of olefins **5a** and **6a**, respectively, readily isolable by chromatography on silica gel impregnated with silver nitrate; while thermal dehydration of 1-cyclohexylcyclopentanol yielded mainly **6a** (80%) [62].

The low regioselectivity observed in the reduction of acetate **4a** resulted from a competition between secondary and tertiary carbon centers to coordinate palladium, i.e. from a π-allyl palladium complex **F** in equilibrium with two σ-allyl palladium complexes **G** and **H**, in which **H** leading to **6a**, would only slightly predominate (see in particular Table 3, entries 1–3) (Scheme 6).

Attempts to reduce 1-acetoxy-1-(1-cyclohexenyl)-cyclopentane (**4b**) ($n = 3$, $m = 2$, X = OAc) [63], either with HCOONa and [15]-crown-5 ether or with n-BuZnCl as hydride sources, in the presence of Pd(dba)$_2$ and PPh$_3$, provided exclusively the conjugated diene, i.e. 1-(1-cyclopentenyl)cyclohexene, resulting from the elimination of 1 equiv. of acetic acid [14], (entries 6, 7).

(For a synthetic route leading to cycloalkylidenecycloalkanes based on the thermal decomposition of β-lactones, see ref. 61).

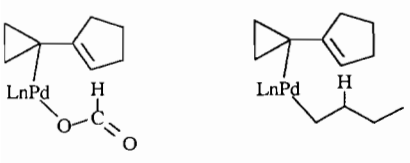
Hydrogenolysis of 1-mesyloxy-1-(1-cyclopentenyl)-cyclopropane (**4c**) ($n=1$, $m=1$, X=OMs), available from cyclopropanone hemiacetal [36, 37] or from 1,3-dichloroacetone [64] by HCOONa and [15]-crown-5 ether, in the presence of $Pd(dba)_2/PPh_3$ provided in 80% yield a 98:2 mixture of cyclopropylidenecyclopentane (**5c**) [65, 66] and 1-cyclopropylcyclopentene (**6c**) [67] (entry 8). On the other hand, hydrogenolysis of **4c** by n-BuZnCl as hydride source, in the presence of $Pd(dba)_2$-PPh_3, yielded exclusively **6c** (83%) (entry 9).

Likewise, 1-mesyloxy-1-(1-cyclohexenyl)cyclopropane (**4d**) ($n=1$, $m=2$) [65], prepared from cyclopropanone hemiacetal [36, 37] or from 1,3-dichloroacetone [64] underwent hydrogenolysis by sodium formate [15]-crown-5 ether in the presence of palladium(0) ($Pd(dba)_2$-$2PPh_3$) to give in 85% yield, a 98:2 mixture of cyclopropylidenecyclohexane (**5d**) [66] and 1-(cyclohexenyl) cyclopropane (**6d**) [67] (entry 10).

Contrary to acetate **4a**, competition between secondary and tertiary carbon centers did not occur with the 1-mesyloxy-1-(1-cycloalkenyl)cyclopropanes (**4c**, **d**). Unsymmetric σ-dimethyleneallyl palladium complexes **I** and **J**, with the palladium clearly positioned on the cyclopropyl carbon, i.e. on the allylic end where the positive charge was less pronounced due to ring strain [10, 43], *vide supra*, were likely the intermediates in hydrogenolysis by sodium formate and n-butylzinc chloride, respectively (Scheme 7).

Once more, comparison of entries 1–3 with 8 and 10, and of entry 4 with 9 in Table 3, clearly illustrated the effect of ring strain on the regioselectivity of the palladium(0) catalyzed hydrogenolysis of allyl esters.

Wittig olefination of aldehydes and ketones by cyclopropylidenetriphenylphosphorane can lead to a wide range of alkylidenecyclopropanes with various yields (45–80%) [66, 68]; however, the reaction did not occur or only in low yields, when the carbonyl compound was readily enolizable. For instance reaction of this ylide with phenylacetaldehyde gave the phenylethylidenecyclopropane **2g** in 9% yield [69] (compare with the Pd(0) catalyzed hydrogenolysis of **1g**, Table 2, entry 6), and with cyclohexanone the cyclopropylidenecyclohexane **5d** [66] in 47% yield based on gas chromatography (compare with Table 3, entry 10). Moreover this cyclopropylphosphorane can readily undergo ring opening; for instance, upon treatment with the sodium salt of salicylaldehyde it gave in 60% yield a 35:65 mixture of 2,3-dihydro-1-benzoxepin and 2-methyl-3-chromene [66]. We had previously reported that Wittig olefination of the cyclopropanone hemiacetal [70] can offer an alternative to the reaction of cyclopropylidenephosphorane to provide cyclopropylidene derivatives, however this olefination required the anchimeric assistance of an electron-donating substituent on the phosphorus ylides and was only effective with arylidenetriphenyl phosphoranes [37, 70], triethylphosphonoacetate [37, 70] or triphenylphosphoranylidene acetates under benzoic catalysis [71].



I J

Scheme 7.

Conclusions

High level of regioselectivity can be reached in the palladium(0) catalyzed hydrogenolysis of allyl esters. This selectivity appeared highly dependent on the difference of positive charge density between the two ends of the allylic systems. However it can be increased either by ring strain, silyl substitution of the allyl moities which readily provide allylsilanes or by using the steric hindrance of the phosphorus ligands. This reduction can then offer an alternative or better a solution to overcome the limitation of the Wittig olefination, due for instance to competitive enolization of the carbonyl moieties, and provide not only mono- (i.e. 1-alkenes) [2a–d], di- (e.g. exo methylenes) [2e] but also readily tri- or tetrasubstituted olefins from 1-(1-alkenyl)- and 1-(1-cycloalkenyl)cycloalkyl esters.

Experimental

General procedure for the preparation of 1-propargylic cycloalkanols

To a stirred solution of 10 mmol of methylmagnesium chloride in 30 ml of THF under argon, was added dropwise at room temperature a solution of 10 mmol of alkyne (1-hexyne, phenylacetylene, trimethylsilylacetylene) in 20 ml of THF. When the addition was over, the resulting solution was heated at reflux for around 1 h, until no gas (CH_4) evolved. The solution was then cooled to 0 °C and 10 mmol of cycloalkanone (cyclohexanone or the magnesium salt of cyclopropanone hemiketal [25]) in 20 ml of THF were added. The mixture was stirred overnight at 50 °C; then after usual work up the solvents were evaporated and the organic phase was purified by chromatography on silica gel (hexane/ether 9:1) to give the corresponding pure propargylic cycloalkanols in 70–90% yields.

Following this method were prepared 1-(1-hexynyl)cyclohexanol [34], 1-(trimethylsilylethynyl)cyclohexanol [17], 1-(trimethylsilylethynyl)cyclopropanol, 1-(1-hexynyl)cyclopropanol and 1-styrylcyclopropanol [9].

1-(Trimethylsilylethynyl)cyclopropanol

Yield 89%; m.p. 35.7 °C. IR (neat): 3400, 3130, 2980, 2920, 2170, 1255 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ: 0.08 (s, 9H), 0.82–0.94 (m, 2H), 0.98–1.05 (m, 2H), 3.98 (broad s, 1H). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: −0.17, 17.38, 45.47, 86.20, 107.69. MS (70 eV) *m/z* (%): 155 (M^+ +1, 3.79), 154 (M^+, 24.8), 134 (49.7), 99 (100), 75 (51.4), 73 (21.4). *Anal.* Calc. for $C_8H_{14}OSi$ (154.28): C, 62.28; H, 9.15. Found: C, 61.87; H, 9.15%.

1-(1-Hexynyl)cyclopropanol

Yield 82%. IR (neat): 3350, 3120, 2980, 2950, 2980 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 0.85–0.93 (m, 5H), 0.99–1.02 (m, 2H), 1.3–1.5 (m, 4H), 2.19 (t, 2H, J=6.8 Hz), 2.63 (broad s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 13.52, 17.02, 18.40, 21.87, 30.71, 45.78, 81.66, 82.88. MS (70 eV) *m/z* (%): 139 (M^++1, 1.75), 138 (M^+, 16.7), 109 (58.4), 96 (100), 95 (78.8), 81 (77.3), 79 (63.8), 67 (73.1), 55 (46.3), 41 (46). *Anal.* Calc. for $C_9H_{14}O$ (138.21): C, 78.21; H, 10.21. Found: C, 78.06; H, 10.28.

*Preparation of the allylic alcohols **1a,b** and **1d–g** (X=OH)*

To a stirred solution of 7.5 mmol (1.5 equiv.) of lithiumaluminum hydride in 30 ml of THF was added dropwise under argon at room temperature a solution of propargylic alcohol in 20 ml THF. After heating at reflux for 2 h, 30 ml of ether were added and the resulting mixture was cooled to 0 °C. Then, wet sodium sulfate was added by portions until no effervescent reaction occurred. After stirring for 2 h, the solution was filtered through celite, dried on anhydrous sodium sulfate, the solvents were evaporated *in vacuo* and the residue was purified by chromatography on silica gel (hexane/ether 9:1) to yield 90–98% of the corresponding allyl alcohols.

Following this method were prepared with X=OH: 1-ethenylcyclohexanol (**1a**) (from commercially available 1-ethynylcyclohexanol) [9a], *E*-1(2-trimethylsilylethenyl)cyclohexanol (**1b**) [17], *E*-1-(1-hexenyl)cyclohexanol (**1d**) [9a], *E*-1-(1-hexenyl)cyclopropanol (**1e**), *E*-1-(2-trimethylsilylethenyl)cyclopropanol (**1f**) and *E*-1-styrylcyclopropanol (**1g**) [10].

E-1-(1-Hexenyl)cyclopropanol (1e) (X=OH)

Yield 95%. IR (neat): 3310, 3100, 3020, 2970, 2940, 2890, 2870, 1675 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 0.63 (dd, 2H, J=7.2 and 2.4 Hz), 0.87 (t, 3H, J=7 Hz), 0.96 (dd, 2H, J=7.2 and 2.4 Hz), 1.24–1.38 (m, 4H), 1.97–2.08 (m, 2H), 2.76 (broad s, 1H), 5.22 (d, 1H, J=16.5 Hz), 5.57–5.72 (1H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 13.95, 15.56, 22.23, 31.71, 55.27, 127.34, 133.54. MS (70 eV) *m/z* (%): 140 (M^+, 0.5), 84 (11), 83 (100), 55 (17.7). *Anal.* Calc. for $C_9H_{16}O$ (140.22): C, 77.09; H, 11.50. Found: C, 76.91; H, 11.47%.

E-1-(2-Trimethylsilylethenyl)cyclopropanol (1f) (X=OH)

Yield 93%. IR (neat): 3310, 3105, 3021, 2970, 2912, 1620, 1305, 1255 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ: 0.07 (s, 9H, $SiMe_3$), 0.78 (dd, 2H, J=7.45 and 4.95 Hz, Cpr-H), 1.11 (dd, 2H, J=7.45 and 4.95 Hz, Cpr-H), 2.30 (m, 1H, OH), 5.68 (d, 1H, J=18.8 Hz), 5.90 (d, 1H, J=18.8 Hz). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: −1.30, 16.24, 56.53, 123.87, 149.85. MS (70 eV) *m/z* (%) 156 (M^+, 1.0), 97 (27.9), 83 (36.7), 82 (40.3), 75 (100), 73 (81.3), 66 (35.5), 59 (25.1), 43 (38.8). *Anal.* Calc. for $C_8H_{16}OSi$ (156.30): C, 61.48; H, 10.32. Found: C, 61.76; H, 10.61%.

Preparation of the allylic alcohol 1c (X=OH)

To a solution of 260 mg (2.1 mmol) of 1-ethynylcyclohexanol in 10 ml of CH_2Cl_2 containing 7 mg (1%) of hexachloroplatinic acid was added dropwise and at room temperature 368 μl (1.1 equiv.) of triethylsilylhydride [20]. After stirring overnight, the solution was concentrated *in vacuo* and purified by chromatography on silica gel (hexane/ether 95:5) to yield 353 mg (70%) of *E*-1-(2-triethylsilylethenyl)cyclohexanol (**1c**) (X=OH) [20].

*Preparation of the allylic alcohols **4a–d** (X=OH)*

To a solution of 10 mmol of 1-lithiocycloalkene (prepared from reaction of chlorocycloalkene with lithium in ether at room temperature [59]) in 30 ml of ether was added dropwise under argon at 20 °C a solution of 10 mmol of ketone (cyclohexanone, cyclopentanone or magnesium salt of cyclopropanone hemiketal [37]) in 20 ml of THF. After stirring overnight and usual work up, the resulting solution was concentrated *in vacuo* and purified by chromatography on silica gel (hexane/ether 9:1) to give the pure expected allylic alcohols in 60–75% yield.

Following this method were prepared with X=OH: 1-(1-cyclopentenyl)cyclohexanol (**4a**) [60], 1-(1-cyclohexenyl)cyclopentanol (**4b**) [63], 1-(1-cyclopentenyl)cyclopropanol (**4d**) [64] (X=OH) and 1-(1-cyclohexenyl)cyclopropanol (**4d**) [64].

*Procedure for the preparation of the acetates **1a–d** and **4a,b** (X=OAc)*

To a solution of 1 mmol of the allylic alcohols **1a–d** (X=OH) and 135 mg (1.1 mmol) of *N*,*N*-dimethyl-

aminopyridine (DMAP) in 5 ml of ether cooled to 0 °C, was added dropwise 140 μl (1.5 mmol) of acetic anhydride. The solution was allowed to warm to room temperature and stirred overnight. The resulting mixture was then concentrated *in vacuo* and the residue was dissolved in hexane, filtered through a sintered glass funnel, concentrated again by removal of solvent *in vacuo* and finally purified by chromatography on silica gel (previously washed by a 2% solution of NEt_3 in hexane) with a 98:2 hexane/ether solution. The acetates were obtained with 70–90% yields.

Following this method were prepared 1-acetoxy-1-ethenylcyclohexane (**1a**) [9b], *E*-1-acetoxy-1-(2-trimethylsilylethenyl)cyclohexane (**1b**), *E*-1-acetoxy-1-(2-triethylsilylethenyl)cyclohexane (**1c**), *E*-1-acetoxy-1-(1-hexenyl)cyclohexane (**1d**), 1-acetoxy-1-(1-cyclopentenyl)cyclohexane (**4a**) and 1-acetoxy-1-(1-cyclohexenyl)-cyclopentane (**4b**).

*1-Acetoxy-1-(2-trimethylsilylethenyl)cyclohexane (**1b**) (X=OAc)*

Yield 82%. IR (neat): 2960, 2880, 1735, 1622, 1250 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ: 0.05 (s, 9H), 1.4–1.6 (m, 8H), 2.01 (s, 3H), 2.1–2.2 (m, 2H), 5.73 (d, 1H, J=19.2 Hz), 6.22 (d, 1H, J=19.2 Hz). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: −1.39, 21.87, 22.02, 25.31, 34.79, 82.55, 127.49, 149.01, 169.44. MS (Cl (NH_3)) *m/z* (%): 258 (M^++18, 1.27), 240 (M^+, 1.83), 181 (100). *Anal.* Calc. for $C_{13}H_{24}O_2Si$ (240.42): C, 64.95; H, 10.06. Found: C, 64.73; H, 9.9%.

*1-Acetoxy-1-(2-triethylsilylethenyl)cyclohexane (**1c**) (X=OAc)*

Yield 85%. IR (neat): 2950, 2890, 1750, 1628, 1235 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 0.55 (q, 6H, J=8 Hz), 0.88 (t, 9H, J=8 Hz), 1.4–1.6 (m, 8H), 1.97 (s, 3H), 2–2.2 (m, 2H), 5.66 (d, 1H, J=19.4 Hz), 6.24 (d, 1H, J=19.4 Hz). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: 3.44, 7.33, 22.13, 25.50, 35.07, 82.69, 123.88, 150.70, 169.46. MS (70 eV) *m/z* (%): 282 (M^+, 1.78), 253 (36.8), 239 (37), 193 (52), 145 (71), 75 (35.9), 59 (100). *Anal.* Calc. for $C_{16}H_{30}O_2Si$ (282.50): C, 68.03; H, 10.70. Found: C, 68.26; H, 10.57%.

*E-1-Acetoxy-1-(1-hexenyl)cyclohexane (**1d**) (X=OAc)*

Yield 84%. IR ($CDCl_3$): 2940, 2870, 1735, 1540, 1340, 1270, 1240 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 0.88 (t, 3H, J=7 Hz), 1.20–1.34 (m, 5H), 1.43–1.63 (m, 7H), 1.99 (s, 3H), 2.02–2.22 (m, 4H), 5.52–5.79 (m, 2H). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: 13.86, 22.04, 22.20, 25.42, 31.29, 32.07, 35.31; 81.74, 130.40, 133.32, 169.78. MS (70 eV) *m/z* (%): 181 (M^+−43, 6.4), 165 (4), 162 (54), 138 (66), 123 (26.4), 120 (17.6), 199 (22.6), 105 (38.3), 93 (20.9), 92 (27.6), 91 (100), 81 (40.7), 80 (51.4), 79 (64.2), 78 (21.1), 77 (42), 65 (29), 67 (44.5), 65 (29), 55 (46.4), 43 (100). *Anal.* Calc. for $C_{14}H_{24}O_2$ (224.34): C, 74.95; H, 10.78. Found: C, 74.82; H, 10.86%.

*1-Acetoxy-1-(1-cyclopentenyl)cyclohexane (**4a**) (X=OAc)*

Yield 79%. IR ($CDCl_3$): 2940, 2860, 1728, 1450, 1370, 1270, 1240 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.23–1.72 (m, 9H), 1.76–1.90 (m, 3H), 2.02 (s, 3H), 2.22–2.38 (m, 4H), 5.53 (t, 1H, J=2Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 21.63, 23.05, 25.45, 31.27, 32.41, 34.46, 81.55, 124.25, 147.21, 169.90. MS (70 eV) *m/z* (%): 149 (M^+−59, 28), 148 (100), 133 (25), 119 (27), 105 (28), 92 (26), 91 (53), 81 (31), 80 (53), 79 (47), 77 (26), 67 (41), 45 (25), 43 (54). *Anal.* Calc. for $C_{13}H_{20}O_2$ (208.30): C, 74.96; H, 9.68. Found: C, 74.90; H, 9.48%.

*1-Acetoxy-1-(1-cyclohexenyl)cyclopentane (**4b**) (X=OAc)*

Yield 76%. IR ($CDCl_3$): 2930, 2880, 2840, 1740, 1645, 1450, 1370, 1250 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ: 1.4–2.5 (m, 19H with s emerging at 1.92), 5.60 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 21.97, 22.74, 23.03, 24.70, 24.86, 36.38, 93.16, 120.65, 138.06, 169.63. MS (70 eV) *m/z* (%): 149 (M^+−59, 23), 148 (100), 133 (40), 120 (24), 119 (35), 107 (36), 105 (43), 92 (35), 91 (73), 81 (28), 80 (58), 79 (70), 78 (26), 77 (34), 67 (51), 60 (20), 45 (30), 43 (67). *Anal.* Calc. for $C_{13}H_{20}O_2$ (208.30): C, 74.96; H, 9.68. Found: C, 74.99; H, 9.54%.

*Preparation of the tosylates **1e–g** (X=OTs)*

To a solution of 10 mmol of the allylic alcohols **1e–g** (X=OH), 1 mmol (0.1 equiv.) of DMAP and 1.53 ml (11 mmol, 1.1 equiv.) of triethylamine in 30 ml of dichloromethane cooled to 0 °C was added dropwise a solution of 2.1 g (11 mmol) of tosylchloride in 20 ml of CH_2Cl_2. The solution was then allowed to warm to room temperature and the reaction was monitored by TLC. When tosylation was complete (about 4 h), the solution was concentrated *in vacuo* and the resulting oil was dissolved in hexane, filtered on celite and dried on anhydrous sodium sulfate. Evaporation of solvent gave the practically pure corresponding allylic tosylates which could be used without purification for further reactions.

Following this method were prepared *E*-1-(1-hexenyl)-1-tosyloxycyclopropane (**1e**) (X=OTs), *E*-1-tosyloxy-1-(2-trimethylsilylethenyl)cyclopropane (**1f**) and *E*-1-styryl-1-tosyloxycyclopropane (**1g**) (X=OTs) [10].

*E-1-(1-Hexenyl)-1-tosyloxycyclopropane (**1e**) (X=OTs)*

Yield 90%. IR ($CDCl_3$): 2980, 2940, 2890, 1660, 1610 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 0.79–0.87 (m, 5H), 1.16–1.31 (m, 6H), 1.86 (m, 2H), 2.41 (s, 3H), 5.50–5.53 (m, 2H), 7.29 (d, 2H, J=8 Hz), 7.73 (d, 2H,

$J=8$ Hz). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: 13.08, 13.80, 21.49, 22.06, 30.77, 31.40, 65.61, 127.10, 127.82, 129.45, 132.06, 135.24, 144.35. MS (70 eV) *m/z* (%): 294 (M^+, 2.22), 122 (36.4), 93 (47.4), 91 (37), 80 (37.6), 79 (100). *Anal.* Calc. for $C_{16}H_{22}O_3S$ (294.41): C, 65.28: H, 7.53; S, 10.89. Found: C, 65.66; H, 7.6; S, 10.23%.

*E-1-Tosyloxy-1-(2-trimethylsilylethenyl)cyclopropane (**1f**) (X=OTs)*

Yield: 67%; m.p. 37.7 °C. IR ($CDCl_3$): 2970, 1625, 1610, 1370, 1255 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: −0.05 (s, 9H), 0.93 (m, 2H), 1.44 (m, 2H), 2.42 (s, 3H), 5.54 (d, 1H, $J=18.8$ Hz), 5.84 (d, 1H, $J=18.8$ Hz), 7.30 (d, 2H, $J=8$ Hz), 7.76 (d, 2H, $J=8$ Hz). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: 3.85, 12.74, 19.59, 64.78, 125.28, 126.04, 127.53, 133.02, 141.29, 142.67. MS (Cl(NH_3)) *m/z* (%): 328 ($M^+ + 18$, 100). *Anal.* Calc. for $C_{15}H_{22}O_3SSi$ (310.48); C, 58.03; H, 7.14; S, 10.33. Found: C, 58.2; H, 7.11; S. 10.54%.

*Preparation of the mesylates **4c** and **4d** (X=OMs)*

To a solution of 4 mmol of allylic alcohols **4c,d** and 1.66 ml (12 mmol, 3 equiv.) of triethylamine in 20 ml of CH_2Cl_2 cooled to 0 °C was added dropwise 0.47 ml (6 mmol, 1.5 equiv.) of methanesulfonyl chloride. When the addition was over the resulting solution was allowed to warm to room temperature and around 2 h later, the reaction was over as monitored by TLC. The solution was then diluted with 20 ml of CH_2Cl_2 and 5 ml of water; the organic phase was successively washed by portions of 2 ml of 0.5 N HCl until acidification, then by saturated sodium bicarbonate and brine. After evaporation of the solvent, *in vacuo*, the residue was dissolved in ether, dried on anhydrous sodium sulfate, filtered and concentrated to provide in good yields (70–90%) the expected mesylates, which then could be used without purification for further reactions.

Following this method were prepared 1-(1-cyclopentenyl)-1-mesyloxycyclopropane (**4c**) (X=OMs) and 1-(1-cyclohexenyl)-1-mesyloxycyclopropane (**4d**) (X=OMs).

*1-(1-Cyclopentenyl)-1-mesyloxycyclopropane (**4c**) (X=OMs)*

Yield 74%. IR ($CDCl_3$): 3080, 3040, 2970, 2835, 1610, 1455, 1425, 1635 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ: 0.98 (m, 2H), 1.18 (m, 2H), 1.90 (m, 2H), 4.07 (t, 4H, $J=7.5$ Hz), 2.96 (s, 3H), 5.74 (m, 1H). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: 12.60, 23.19, 32.29, 32.37, 39.29, 64.30, 128.29, 141.04. MS (70 eV) *m/z* (%): 202 (M^+, 9.3), 106 (46), 105 (29), 95 (100), 91 (82), 81 (44), 79 (46), 78 (38), 67 (67), 66 (26), 65 (36), 41 (66), 39 (61).

*1-(1-Cyclohexenyl)-1-mesyloxycyclopropane (**4d**) (X=OMs)*

Yield 75%. IR (neat): 3120, 3040, 2950, 2870, 1675, 1365 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ: 0.93 (dd, 2H, $J=7.7$ and 6.3 Hz), 1.33 (dd, 2H, $J=7.7$ and 6.3 Hz) 1.55–1.70 (m, 4H), 2.06–2.09 (m, 2H), 2.15–2.21 (m, 2H), 2.97 (s, 3H), 5.99 (m, 1H). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: 11.59, 21.90, 22.31, 24.87, 25.53, 39.23, 69.41, 128.26, 133.59. MS (70 eV) *m/z* (%): 216 (M^+, 5.7), 105 (100), 92 (66.5), 91 (67.7), 79 (67.7), 78 (32.8), 77 (34.6). *Anal.* Calc. for $C_{10}H_{16}O_3S$ (216.29): C, 55.53; H, 7.41. Found: C, 55.86; H, 7.23%.

General procedure for the palladium(0) catalyzed reduction of allylic esters

(a) Preparation of the π(1,1-polymethylene)allyl palladium(0) complex

A solution of 0.5 mmol of the allylic esters **1a–g** in 2 ml of THF was stirred under argon with a solution of 15 mg (0.025 mmol) (5%) of palladium dibenzylideneacetone ($Pd(dba)_2$) and 0.05 mmol (10%) of phosphine ligand (6% of bidentate phosphine ligand such as dppe, were used) in 2 ml of THF. After stirring at room temperature for 15–45 min, the orange coloration of the mixture observed with tosylates and mesylates disappeared and the resulting solution could then be used for the reduction reaction.

(b) Reduction by sodium formate and [15]-crown-5 ether

In a flask containing 102 mg (1.5 mmol, 3 equiv.) of sodium formate and 11 mg (10%) of [15]-crown-5 ether was added the solution of the palladium complex prepared as reported above. The mixture from acetates **1a–d** was then heated at reflux for 1–15 h until the complete disappearance of the starting material as monitored by TLC; reaction of tosylates **1e–g** and mesylates **4c,d** was complete at room temperature within 12 h. After cooling the mixture to room temperature, 30 ml of pentane or hexane and 5 ml water were added and after filtration through celite, the organic phase was washed several times by water, dried on anhydrous sodium sulfate and purified by chromatography on silica gel (elution with pentane or hexane) to yield after evaporation of solvent *in vacuo* the reduced products.

(c) Reduction by n-butylzinc chloride

A 0.3 M THF solution of n-butylzinc chloride (prepared *in situ* from a mixture of n-butyllithium and zinc dichloride) was added to the solution of the π-(1,1-polymethylene)allyl palladium(0) complex prepared as reported above. The mixture was then stirred at room temperature for 1–3 h until the starting esters had completely disappeared as monitored by TLC. (In rare cases, heating at reflux for a very short time was

necessary.) The work-up as described above for the reduction by sodium formate was then applied to obtain the reduction products.

From 1-acetoxy-1-ethenylcyclohexane (**1a**) (X = OAc) were obtained ethylidene cyclohexane (**2a**) [11] (identified by one ^{1}H NMR vinylic proton at δ 5.1 ppm (q, J = 7 Hz)) and ethenylcyclohexane (**3a**) [12] (identified by two vinylic protons at δ 4.9 (m) and 5.8 ppm (m)); from *E*-1-acetoxy-1-(2-trimethylsilylethenyl)cyclohexane (**1b**) (X = OAc) were obtained 2-(trimethylsilylethylidene)cyclohexane (**2b**) [18] (identified by one ^{1}H NMR vinylic proton signal triplet at δ 5.09 ppm (t, J = 8.56 Hz)) and *E*-2-(trimethylsilylethenyl)-cyclohexane (**3b**) [19] (identified by two vinylic protons at δ 5.38 (dd, J = 18.80 and 1.28 Hz) and 5.97 ppm (dd, J = 18.80 and 5.87 Hz)); from *E*-1-acetoxy-1-(2-triethylsilylethenyl)cyclohexane (**1c**) (X = OAc) were obtained 2-(triethylsilylethylidene)cyclohexane (**2c**) [21] (identified by one ^{1}H NMR vinylic proton signal triplet at δ 5.09 ppm (t, J = 8.5 Hz)) and *E*-2-(triethylsilyl-ethenyl)cyclohexane (**3c**) [22] (identified by two vinylic protons at δ 5.48 (dd, J = 18.93 and 1.23 Hz) and 5.98 ppm (dd, J = 18.93 and 6.09 Hz)); from *E*-1-acetoxy-(1-hexenyl)cyclohexane (**1d**) (X = OAc) were obtained hexylidenecyclohexane (**2d**) [9b] (evidenced by one ^{1}H NMR single vinylic proton at δ 5.07 ppm (t, J = 8.6 Hz)) and *E*-(1-hexenyl)cyclohexane (**3d**) [9b] (evidenced by two vinylic protons at δ 5.34 (m) ppm); and from *E*-1-(1-hexenyl)-1-tosyloxycyclopropane (**1e**) (X = OTs) were obtained hexylidenecyclopropane (**2e**) [38] (identified by a single ^{1}H NMR vinylic proton at δ 5.19 ppm (t, J = 6 Hz)) and *E*-(1-hexenyl)cyclopropane (**3e**), with the ratios reported in Table 1.

E-(1-hexenyl)cyclopropane (3e)

IR ($CDCl_3$): 3100, 3112, 2980, 2950, 2880, 1615 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.28–0.34 (m, 2H), 0.61–0.67 (m, 2H), 0.89 (t, 3H, J = 7 Hz), 1.27–1.36 (m, 4H), 1.84–2.21 (m, 3H), 4.95 (dd, 1H, J = 15.2 and 8.6 Hz), 5.51 (dt, 1H, J = 15.2 and 7 Hz). ^{13}C NMR (62.8 MHz, $CDCl_3$) δ: 6.33, 13.49, 13.96, 22.22, 31.59, 31.87, 128.29, 133.59. MS (70 eV) *m/z* (%): 125 (M^+ + 1, 2.2), 124 (M^+, 26.7), 95 (26.1), 82 (30.6), 81 (94.9), 79 (51.4), 68 (79.8), 67 (100), 54 (37.2), 41 (37.7).

From *E*-1-tosyloxy-1-(2-trimethylsilylethenyl)cyclopropane (**1f** (X = OTs) were obtained (2-trimethylsilyl-ethylidene)cyclopropane (**2f**) and *E*-(2-trimethylsilyl-ethenyl)cyclopropane (**3f**); and from *E*-1-tosyloxy-1-styrylcyclopropane (**1g**) (X = OTs) were obtained benzylidenecyclopropane (**2g**) [10] (evidenced by a single ^{1}H NMR vinylic proton at δ 5.95 (m) ppm) and *E*-styrylcyclopropane (**3g**) [45] (evidenced by two vinylic protons at δ 5.72 (dd, J = 15.6 and 8.8 Hz) and 6.47 ppm (d, J = 15.6 Hz)), with the ratios reported in Table 1.

(2-Trimethylsilylethylidene)cyclopropane (2f)

IR ($CDCl_3$): 3060, 3000, 2980, 2920, 1420, 1340, 1255 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.01 (s, 9H), 0.92–0.98 (m, 2H), 1.03–1.09 (m, 2H), 1.58 (d, 2H, J = 8 Hz), 5.74 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 1.79, 1.82, 2.83, 21.97, 114.51, 118.98. MS (70 eV) *m/z* (%): 140 (M^+, 0.4), 75 (5.1), 74 (15.5), 73 (100), 45 (5.25). *Anal.* Calc. for $C_8H_{16}Si$ (140.30): C, 68.49; H, 11.49. Found: C, 68.21; H, 11.67%.

E-(2-Trimethylsilylethenyl)cyclopropane (3f)

IR ($CDCl_3$): 3100, 3020, 2980, 2920, 1620, 1360, 1255 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.04 (s, 9H), 0.43–0.48 (m, 2H), 0.70–0.80 (m, 2H), 1.41–1.55 (m, 1H), 5.46 (dd, 1H, J = 18.4 and 8.4 Hz), 5.71 (d, 1H, J = 18.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ: −1.14, 7.24, 17.41, 126.52, 150.73. MS (70 eV) *m/z* (%): 140 (M^+, 7.6), 75 (5.1), 125 (46.6), 123 (21.2), 97 (27.3), 73 (57.5), 59 (100), 45 (23), 43 (21.5). *Anal.* Calc. for $C_8H_{16}Si$ (140.30): C, 68.49; H, 11.49. Found: C, 68.27: H, 11.52%.

From 1-acetoxy-1-(1-cyclopentenyl)cyclohexane (**4a**) (X = OAc) were obtained cyclopentylidenecyclohexane (**5a**) [61] and 1-(1-cyclopentenyl)cyclohexane (**6a**) (exhibiting among others one ^{1}H NMR vinylic proton at δ 5.30 (m) ppm [62]); from 1-mesyloxy-(1-cyclopentenyl)cyclopropane (**4c**) (X = OMS) were obtained cyclopropylidenecyclopentane (**5c**) [66] and 1-(1-cyclopentenyl)cyclopropane (**6c**) (evidenced by one ^{1}H NMR vinylic proton at δ 5.56 (m) ppm [67]), and from 1-mesyloxy-(1-cyclohexenyl)cyclopropane (**4d**) (X = OMs) were obtained cyclopropylidenecyclohexane (**5d**) [66] and 1-(1-cyclohexenyl)cyclopropane (**6d**) [67] (evidenced by one ^{1}H NMR vinylic proton at δ 5.43 (br s) ppm), with ratios depending on the Pd(0) phosphine ligand as reported in Table 3.

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