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Stereoselectivity of the Carbopalladation-Functionalization of Allenic Compounds : a Mechanistic Study.

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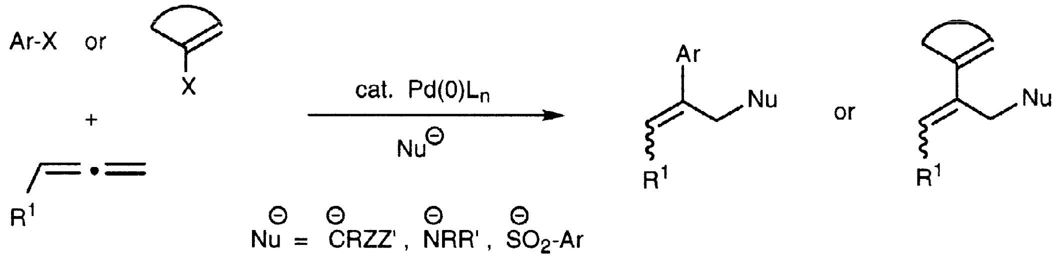
Abstract : A comparison between the stereo-outcome of the carbopalladation-functionalization of monosubstituted allenes and the palladium-catalyzed substitution of dienic acetates **1** and **4** by a malonate anion shows that the same π-allyl intermediate should be involved in both processes. During this study, an influence of the counter-ion of the palladium complex on the stereoselectivity of the process was clearly demonstrated. © 1998 Elsevier Science Ltd. All rights reserved.

Results from our group[1-4] and others[5] have shown that the carbopalladation of allenic compounds with a σ-arylic or σ-vinylic palladium complex in the presence of a stabilized carbon nucleophile or heteroatom nucleophile constitutes a straightforward route to dienic or styrenic compounds bearing a functionalized substituent (scheme 1).



<scheme 1>

This reaction is generally highly regioselective with attack of the nucleophile on the terminal carbon of the allenic unit. It also exhibits high stereoselectivity with the favored formation of a E double bond when aryl or "hindered" unsaturated halides (i.e.: 2-bromopropene, 1-bromocyclohexene and cyclopentene, etc) are used. On the contrary, the reaction looses its stereoselectivity when "unhindered" unsaturated halides (i.e.: vinylbromide, (E)-1-bromopropene) are used and gives roughly an equimolecular mixture of E and Z isomers.[1-3] However, the reaction can be completely Z-stereoselective when σ-ethynylpalladium species (formed from the corresponding acetylenic bromides) were used in order to make conjugated enynes.[6]

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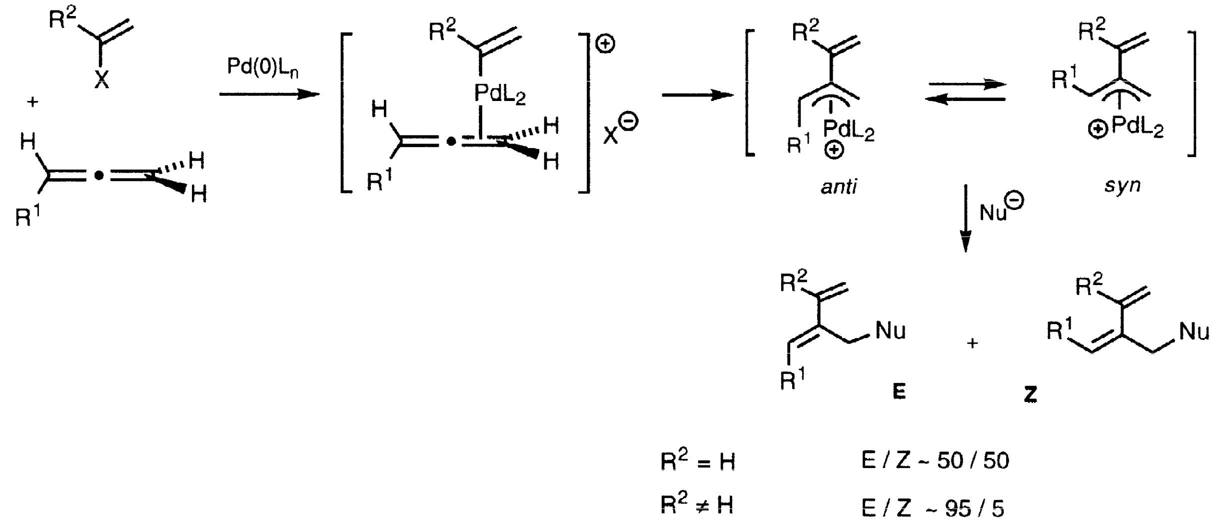
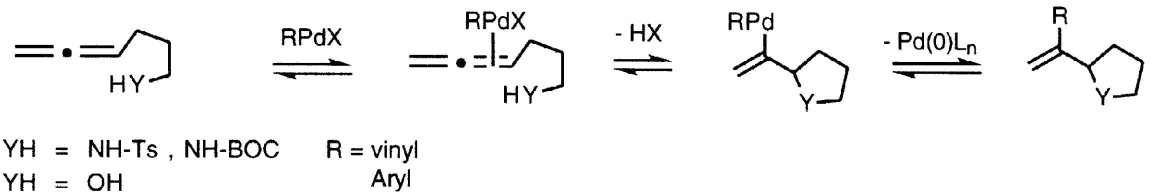
Based on our results[1-3] and on previous results described in the literature,[7] we have proposed for this three-partner reaction a two-step mechanism involving of a π-allylpalladium complex resulting from the addition of σ-unsaturated (aryl or vinyl)palladium species onto the allenic moiety (scheme 2). With monosubstituted allenes ($R^1 \neq H$), this π-allylpalladium intermediate can exist in two different configurations, *syn* and *anti*, which are respectively transformed to the Z and E isomers of the terminal product by attack of the nucleophile.



<scheme 2>

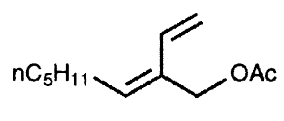
The palladium-catalyzed carbon-carbon bond formation occurs preferentially on the less sterically hindered face of the terminal double bond[8] of the allenic unit, giving the *anti* π-allylpalladium which equilibrates with its *syn* isomer. The relative stabilities of these two complexes are responsible of the stereo-outcome of the whole process : when $R^2 \neq H$, the *anti* isomer is the more stable due to the lack of steric interactions between R^1 and R^2 or R^1 and the vinyl group. When R^2 is an hydrogen, these interactions are smaller and thus both π-allyl complexes have about the same stabilities. When the vinyl group is replaced by an ethynyl group, those interactions are still smaller so that the *syn* isomer is more stable resulting in only the Z-isomer of the enyne.[6]

Even if the mechanism depicted in scheme 2 seems well supported by experimental arguments,[1-3] it has been questionned by other groups.[9,10] Theses authors have reported a related cyclisation-coupling sequence starting from γ-amino[9] or γ-hydroxy[10] allenes (scheme 3). They proposed a mechanism for this intramolecular sequence which would involve the π-complexation of an alkenylpalladium(II) halide species to the allenic unit followed by the nucleophilic attack of the heteroatom and reductive elimination leading to the final α-alkenyl heterocycle.

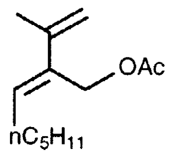


<scheme 3>

Consequently, we tried to obtain further evidence by studying the palladium-catalyzed substitution of dienic acetates **1** and **4**, the preparation of which was described elsewhere.[11]



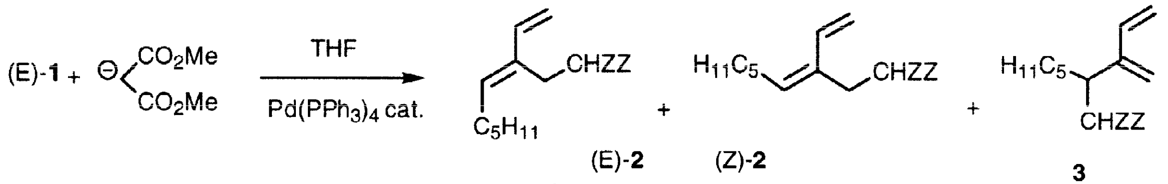
(E)-**1**



(Z)-**4**

I. Palladium-catalyzed substitution of dienic acetate (E)-1.

The reaction of dienic acetate **1** (exclusively E) with the sodium enolate of dimethyl malonate in THF and in the presence of 0.04 equivalent of $Pd(PPh_3)_4$ needs 48 h at 40 °C to be complete. It leads then to a mixture of three isomers, malonates (E)- and (Z)-**2** and the regioisomer **3** (scheme 4) separated by flash chromatography and identified by comparison of their spectra with those of homologs previously described.[1b,2] As in the case of allenic compounds, the reaction is highly regioselective giving the product of direct substitution which corresponds to the attack of the nucleophile on the less substituted carbon of the intermediate π-allylpalladium complex. The stereoselectivity is low (E/Z = 33/67) due to an important isomerization of the starting double bond, the amount of which increases when the reaction is run at higher temperature (65 °C).



(E)-**2** (Z)-**2** **3**

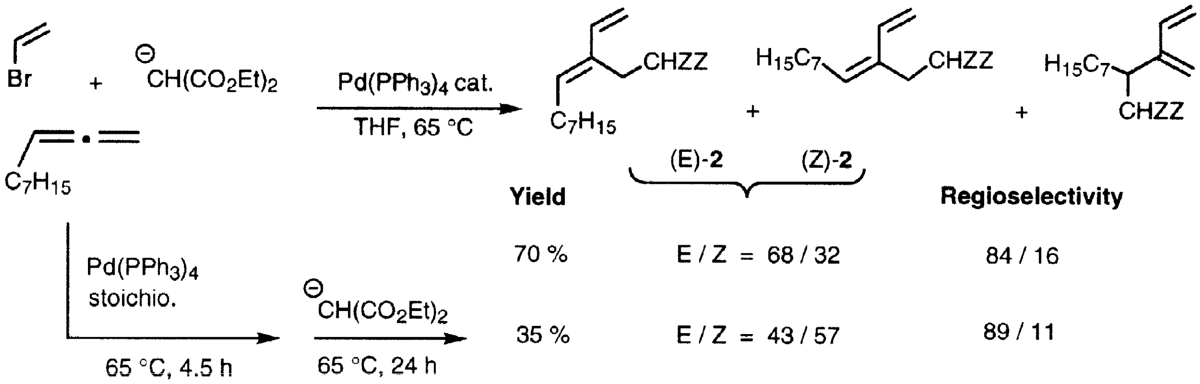
(Z = CO_2Me)

	Yield	(E)-**2** / (Z)-**2**	**2 / 3***
40 °C - 48 h	55 %	E / Z* = 33 / 67	90 / 10
65 °C - 24 h	69 %	E / Z = 46 / 54	89 / 11

* Stereoselectivity (E/Z) and regioselectivity (**2**/**3**) were determined via GLC analysis (idem in scheme 6)

<scheme 4>

These results fit particularly well with those obtained formerly[2] from the carbopalladation-functionalization of deca-1,2-diene with vinylbromide in the presence of $Pd(PPh_3)_4$ in THF at 65 °C which afforded the same kind of mixture with a stereoselection E/Z of 68/32 in a palladium-catalyzed process. When the reaction was carried out with a stoichiometric amount of Pd(0) and a delay of 4.5 hours before the introduction of the nucleophile for the *syn-anti* equilibrium of π-allyl palladium complexes to be complete, the E/Z ratio was 43/57 (scheme 5).[2]

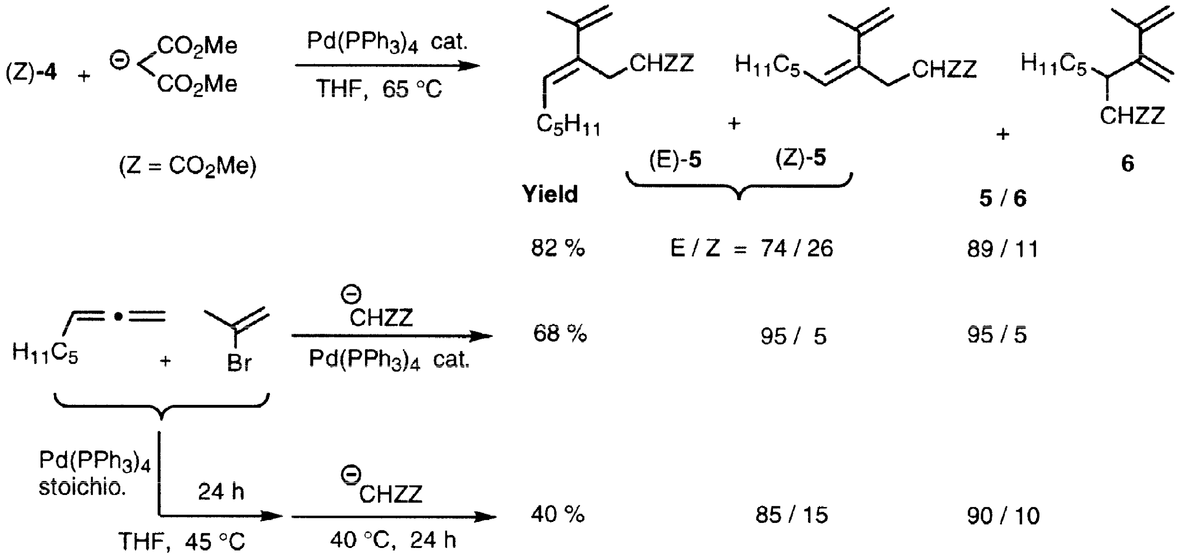


<scheme 5 >

The comparison between these two series of results (Schemes 4 and 5) shows that this equilibrium is not reached quickly : the reaction at 40 °C starting from acetate (E)-**1** gives a 33/67 E/Z ratio intermediate between the kinetic product (*syn* complex generated from (E)-**1** leading consequently to (Z)-**2** isomer) and the thermodynamic mixture, the composition of which is given by the stoichiometric assay of scheme 5 (and the reaction of scheme 4 with (E)-**1** at 65 °C). Similarly, the palladium-catalyzed reaction with deca-1,2-diene (scheme 5) shows an E/Z distribution somewhere between kinetic [*anti* complex and consequently diene (E)-**2**] and thermodynamic control.[1,2] Lastly, the comparison between the results from the allenic hydrocarbon and acetate **1** is in accordance with the involvement in both case of the same π-allylpalladium complex which is probably formed more quickly from **1** than from an allene.

II. Palladium-catalyzed substitution of dienic acetate (Z)-4.

The same comparison was made concerning on one hand, the palladium-catalyzed reaction run with dienic acetate (Z)-**4** and, on the other hand, the palladium-catalyzed reaction as well as the stoichiometric process run with octa-1,2-diene and 2-bromopropene (scheme 6).



<scheme 6>

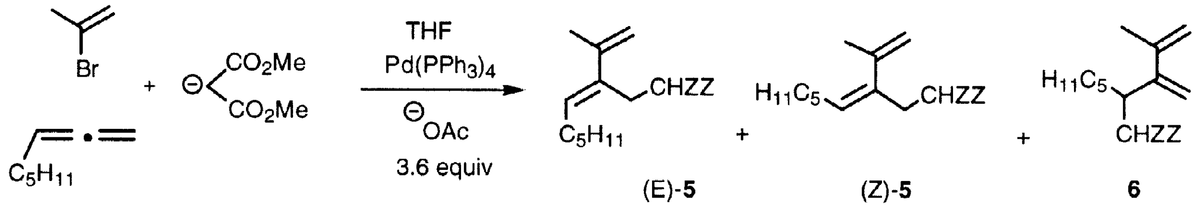
We already reported[2] that the stoichiometric process has a lower yield (40 %) than its catalytic counterpart (70-80 %) due probably to a certain instability of the organopalladium intermediate at high concentration. For that reason, this reaction was run at 40 °C in place of 65 °C.

Results in scheme 6 show some discrepancies in the stereoselectivity of the reactions. Concerning the allene reactions, it is apparent that the catalyzed process is mostly under kinetic control if we consider that the stoichiometric reaction gives a mixture with a composition reflecting the relative stability of both *syn* and *anti* π-allyl complexes (85/15). Then, the result of the reaction of acetate (Z)-**4** seems abnormal (E/Z = 74/26) since, with the initial Z configuration of this compound, we could expect to form initially the ***anti*** isomer of the π-allyl intermediate and recover almost exclusively the diene (E)-**5**.

Influence of the counter-anion on the stereoselectivity.

We suspected that this unexpected low stereoselectivity was due to the change of counter-ion in the π-allyl complex, acetate in the case of **4** as starting material and bromine in that of the carbopalladation-functionalization of octa-1,2-diene. Such counter-ion effect in some palladium-catalyzed reactions have been described and discussed recently.[12] Consequently, the carbopalladation-functionalization of this allenic hydrocarbon with 2-bromopropene (1.2 equiv) was reinvestigated in the presence of sodium acetate or tetra-alkylammonium acetate. The results of these experiments are summarized in Table 1.

Table 1



Entry	$Pd(PPh_3)_4$	Acetate 3.6 equiv	T °C	Time	Yield % (5 + 6)	E / Z[c]	5 / 6[c]
1[d]	5 %	NaOAc	45 °C	30 min (10% conversion)		80 / 20	
			-	1.5 h (16 %)		85 / 15	
			-	3 h (42 %)		90 / 10	
			-	48 h (100 %)	71[a]	91 / 9	88 / 12
2	5 %	NBu_4OAc	45 °C	48 h	65[a]	92 / 8	87 / 13
3	5 %	NMe_4OAc	20 °C	72 h	45[b]	80 / 20	90 / 10
4[e]	100 %	NaOAc	45 °C	24 h	51[b]	80 / 20	90 / 10

a Yields refer to isolated material by flash chromatography.
b GLC yields ($C_{16}H_{34}$ as internal standard).
c E/Z ratio and regioselectivity were determined by GLC analysis.
d Reaction was followed by GLC.
e Dimethyl sodiomalonate was added after stirring the intermediate palladium complex overnight at 45 °C.

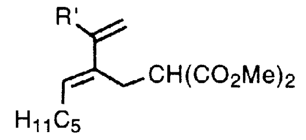
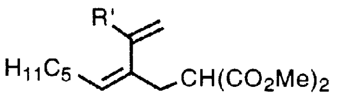
It becomes clear from these four reactions that a counter-ion effect is involved in the stereochemistry of the reaction since the exchange between bromine and acetate reduces the stereoselectivity. At 45 °C the stereoselectivity is quite similar to that observed in the absence of the acetate anion (entries 1 and 2) ; however it was shown to decrease from 80/20 at the begining of the reaction (10 % conversion) to 91/9 at the end as a result of the increase of bromide anion in the reaction mixture (entry 1). In the presence of tetramethylammonium acetate at 20 °C, it is close (E/Z = 80/20) to the one observed (75/25) in the reaction of dienic acetate (Z)-**4**. Fortunately, the influence of the temperature on the kinetics of the nucleophilic attack is large enough to leave the intervention of the bromide-acetate exchange at 20 °C (entry 3). Trapping of the palladium intermediate, stoichiometrically generated in the presence of excess acetate anion, led also to the same lower stereoselectivity (E/Z = 80/20) (entry 4).

III. Stereochemical assigment of dienic malonates 2,5.

Structures of malonates **2**,**3**,**5** and **6** were easily established from their ^{1}H and ^{13}C NMR spectra which were consistent with the ones of analogous malonates or acetylacetates formerly obtained in several previous works.[1b,2,4a] Particularly, the stereochemistry of dienic malonates **2** and **5** was deduced from the comparison of the chemical shift in ^{13}C NMR spectroscopy of the allylic methylene carbon atom $\underline{C}H_2$-$CH(CO_2Me)_2$ which was upshielded (25-27 ppm) in the E-stereoisomer (32-36 ppm in the Z-stereoisomer) because of a positiv cis-γ effect from the allylic carbon atom of the C_5H_{11} alkyl chain[1b] (Table 2).

Table 2

Chemical shift in ^{13}C NMR of methylene carbon $\underline{C}H_2$-$CH(CO_2Me)_2$

			 (E)-**2**,**5**		 (Z)-**2**,**5**
2	R' = H	δ_E	25.5 ppm	δ_Z	32.7 ppm
5	R' = CH_3		26.7 -		35.5 -

In conclusion, this study has brought some additional information about the mechanism of the carbopalladation of allenic compounds. The comparison of the results observed with monosubstituted allenes and those obtained in the same kind of reactions run with dienic acetates **1** and **4** shows that, in both cases, the intermediate of the same π-allyl palladium complexes is highly probable. Recent work by Negishi *et al* about cyclic carbopalladation from ω-haloallenes also supports this mechanism.[13] Moreover, we have noticed a clear effect of the π-allyl complex counter-ion on the stereoselectivity associated with the attack of carbonucleophiles.

EXPERIMENTAL SECTION

General remarks : see preceeding article in this issue.

Materials. Dienic acetates (E)-**1** and (Z)-**4** were prepared from the corresponding dienic alcohols.[11] Octa-1,2-diene[14] and tetrakis(triphenylphosphine)palladium[15] were obtained according to literature procedures.

Palladium-catalyzed substitution of dienic acetate (E)-**1**.

Reaction at 40 °C.

To a solution of complex $Pd(PPh_3)_4$ (115.9 mg, 0.1 mmol) in anhydrous THF (5 mL) at room temperature under N_2 atmosphere, acetate (E)-**1** (390 mg, 2 mmol) was added with a syringe. A solution of dimethyl sodiomalonate freshly prepared from dimethyl malonate (528 mg, 4 mmol, 4 equiv) and NaH (60 % in mineral oil, washed with petroleum ether ; 160 mg, 4 mmol) in THF (10 mL) was transfered *via* a cannula. The reaction mixture was stirred at 40 °C for 48 h. After hydrolysis with saturated NH_4Cl, workup included extraction with ether (3 x 50 mL), washing with water and drying over $MgSO_4$. Evaporation of solvents and short filtration through silica gel (5 g, eluent PE) gave a crude oil [GLC analysis : (E)-**2** : (Z)-**2** : **3** = 30/60/10]. Purification by flash chromatography (65 g SiO_2, 95:5 PE/EtOAc) afforded malonate (E)-**2** (90 mg), malonate (Z)-**2** (178 mg) and the regioisomer **3** (24 mg) with a total yield of 55 %.

(E)-Dimethyl 2-(2-vinyloct-2-enyl)malonate 2.

TLC analysis (SiO_2, 90:10 PE/EtOAc) $R_f = 0.36$.

IR (film) : 3080, 1750, 1720, 1645, 1595, 1440, 1360, 1250, 1150, 990, 900 cm^{-1}

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.57 (t, J = 7.5 Hz, 1H, CH_2-C$\underline{H}$=C), 5.07 (d, J = 17.6 Hz, 1H, CH=C$\underline{H}$H), 4.96 (d, J = 10.9 Hz, 1H, CH=CH$\underline{H}$), 3.72 (s, 6H, 2 O-CH_3), 3.60 (t, J = 7.5 Hz, 1H, C$\underline{H}$($CO_2CH_3)_2$), 2.89 (d, J = 7.5 Hz, 2H, C$\underline{H}_2$-CH), 2.12 (dt, J = 7.5 and 7.2 Hz, 2H, C$\underline{H}_2$-CH=C), 1.17-1.42 (m, 6H, $(CH_2)_3$), 0.88 (t, J = 6.6 Hz, 3H, C$\underline{H}_3$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 169.7 (2 CO), 139.4 (CH_2-$\underline{C}$H=C), 136.8 (H$\underline{C}$=CH_2), 133.7 (HC=$\underline{C}$-CH=C), 111.0 (CH=$\underline{C}H_2$), 52.5 (2 O-$\underline{C}H_3$), 50.5 (CH_2-$\underline{C}$H), 31.6 ($\underline{C}H_2$), 29.2 ($\underline{C}H_2$), 28.2 ($\underline{C}H_2$-CH=C), 25.5 (CH=C-$\underline{C}H_2$), 22.6 ($\underline{C}H_2$), 14.0 ($\underline{C}H_3$).

Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14 ; H, 9.01. Found : C, 67.55 ; H, 9.33.

Malonate (Z)-2.

^{1}H NMR (200 MHz, $CDCl_3$) δ 6.61 (dd, J = 11.1 and 17.6 Hz, C$\underline{H}$=CH_2), 5.45 (t, J = 7.4 Hz, 1H, CH_2-C$\underline{H}$=C), 5.22 (d, J = 17.6 Hz, 1H, CH=C$\underline{H}$H), 5.12 (d, J = 11.1 Hz, CH=C$\underline{H}$H), 3.71 (s, 6H, 2 O-CH_3), 3.64 (t, J = 7.6 Hz, 1H, CH_2-C$\underline{H}$), 2.82 (d, J = 7.5 Hz, 2H, C$\underline{H}_2$-CH), 2.11 (dt, J = 6.8 and 7.4 Hz, 2H, C$\underline{H}_2$-CH=C), 1.15-1.4 (m, 6H, (C$\underline{H}_2)_3$), 0.87 (t, J = 6.4 Hz, 3H, C$\underline{H}_3$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 169.6 (2 CO), 133.9 (CH_2-$\underline{C}$H=C), 132.2 (CH=$\underline{C}$-CH=C), 131.8 ($\underline{C}$H=CH_2), 113.5 (CH=$\underline{C}H_2$), 52.4 (2 O-$\underline{C}H_3$), 51.1 (CH_2-$\underline{C}$H-), 32.7 (C=C-$\underline{C}H_2$-CH), 31.4 ($\underline{C}H_2$), 29.3 ($\underline{C}H_2$), 27.4 ($\underline{C}H_2$-CH=C), 22.5 ($\underline{C}H_2$), 14.0 ($\underline{C}H_3$).

Dimethyl 2-(2-vinyloct-1-en-3-yl)malonate 3.

IR (film) : 3080, 2920, 1740, 1640, 1590, 1470, 1360, 1150, 910 cm^{-1}

^{1}H NMR (200 MHz, $CDCl_3$) δ 6.32 (dd, *J* = 10.9 and 17.5 Hz, 1H, $C\underline{H}=CH_2$), 5.4 (d, *J* = 17.5 Hz, 1H, $CH=C\underline{H}H$), 5.19 (s, 1H, $C=C\underline{H}H$), 5.10 (d, J = 10.8 Hz, $CH=C\underline{H}H$), 4.98 (s, 1H, $C=C\underline{H}H$), 3.75 (s, 3H, $O\text{-}CH_3$), 3.72 (s, 3H, $O\text{-}CH_3$), 3.53 (d, *J* = 10.3 Hz, $C\underline{H}(CO_2CH_3)_2$), 3.19 (td, *J* = 4.1 and 10.3 Hz, 1H, $C\underline{H}\text{-}CH(CO_2)_2$), 1.25-1.40 (m, 8H, $(CH_2)_4$), 0.85 (t, *J* = 6.3 Hz, 3H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$) δ 169.6 (2 CO), 146.6 ($CH\text{-}\underline{C}=CH_2$), 137.8 ($\underline{C}H=CH_2$), 113.9 ($C=\underline{C}H_2$), 114.3 ($C=\underline{C}H_2$), 56.9 ($\underline{C}H(CO_2CH_3)_2$), 52.4 (2 $O\text{-}\underline{C}H_3$), 40.5 ($\text{-}\underline{C}H\text{-}C=CH_2$), 32.2 ($\underline{C}H_2$), 31.4 ($\underline{C}H_2$), 26.3 ($\underline{C}H_2$), 23.9 ($\underline{C}H_2$), 14.0 ($\underline{C}H_3$).

Reaction at 65 °C.

A similar reaction was realized at 65 °C with acetate (E)-**1** (239 mg,1.23 mmol) in the presence of $Pd(PPh_3)_4$ (142 mg, 0.12 mmol). After refluxing during 24 h, the same workup gave a crude oil [GLC analysis : (E)-**2** : (Z)-**2** : **3** = 41/48/11]. Short path chromatography afforded a mixture of regioisomer malonates **2** and **3** (222 mg, 69 %).

Palladium-catalyzed substitution of dienic acetate (Z)-**4**.

A solution of dimethyl sodiomalonate (3 mmol, 1.2 equiv) in THF (10 mL) was transferred *via* a cannula into a solution of $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) and acetate (Z)-**4** (420 mg, 2 mmol) in THF (5 mL) under nitrogen. The reaction mixture was stirred at 40 °C for one day. After workup, evaporation of solvents and short filtration through silica gel gave a crude oil [GLC analysis : (E)-**5** : (Z)-**5** : **6** = 66/23/11]. Purification by flash chromatography (80 g SiO_2, 97:3 PE/EtOAc) afforded malonate (E)-**5** (150 mg), malonate (Z)-**5** (555 mg) and regioisomer **6** (23 mg) with a total yield of 82 %.

(E)-Dimethyl 2-[2-(prop-1-en-2-yl)oct-2-enyl]malonate 5.

IR (film) : 3080, 2920, 2840, 1740, 1605, 1430, 1340, 1230, 1150, 1050, 890 cm^{-1}

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.64 (t, *J* = 7.3 Hz, 1H, $\underline{C}H_2\text{-}C\underline{H}=C$), 4.92 (s, 2H, $CH=C\underline{H}_2$), 3.70 (s, 6H, 2 $OC\underline{H}_3$), 3.58 (t, *J* = 7.5 Hz, 1H, $CH_2\text{-}C\underline{H}$), 2.94 (d, *J* = 7.5 Hz, 1H, $C\underline{H}_2\text{-}CH$), 2.12 (dt, *J* = 7.0 Hz and 7.2 Hz, 2H, $C\underline{H}_2\text{-}CH=C$), 1.86 (s, 3H, $C\underline{H}_3\text{-}C=C$), 1.26-1.43 (m, 6H, $(C\underline{H}_2)_3$), 0.89 (t, 6.6 Hz, $C\underline{H}_3$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 169.8 (2 CO), 142.8 ($CH_3\text{-}\underline{C}=C$), 135.3 ($HC=\underline{C}\text{-}C=C$); 131.6 ($\underline{C}H=C$); 111.4 ($C=\underline{C}H_2$); 42.4 ($O\text{-}\underline{C}H_3$); 50.8 ($\underline{C}H[CO_2CH_3]_2$), 31.6 ($\underline{C}H_2$), 29.5 ($\underline{C}H_2$), 28.4 ($\underline{C}H_2\text{-}CH=C$), 26.7 ($\underline{C}H_2\text{-}CH$), 22.6 ($\underline{C}H_2$), 21.52 ($\underline{C}H_3\text{-}C=C$), 14.0 ($\underline{C}H_3$).

MS (m/z, %) : 282 ($M^{+\bullet}$, 10), 264 (21), 121 (23), 108 (21), 107 (46), 105 (24), 33 (100), 91 (32), 79 (33), 77 (24), 55 (29).

Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.06 ; H, 9.28. Found : C, 67.72 ; H, 8.83.

Malonate (Z)-5.

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.22 (t, *J* = 7.2 Hz, 1H, $CH_2\text{-}C\underline{H}=C$), 4.66 (broad s, 2H, $C=C\underline{H}_2$), 3.7 (s, 6H, 2 $COOC\underline{H}_3$), 3.52 (t, *J* = 7.5 Hz, 1H, $CH_2\text{-}C\underline{H}$), 2.67 (d, *J* = 7.5 Hz, 2H, $C\underline{H}_2\text{-}CH$), 1.98 (dt, *J* = 6.7 and 7.2 Hz, 2H, $C\underline{H}_2\text{-}CH=C$), 1.77 (s, 3H, $C\underline{H}_3\text{-}C=C$), 1.25-1.45 (m, 6H, $(C\underline{H}_2)_3$), 0.89 (t, *J* = 6.6 Hz, 3H, $C\underline{H}_3$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 196.6 (2 CO), 138.3 (CH_3-$\underline{C}$=C), 52.4 (2 O-$\underline{C}H_3$), 50.8 ($\underline{C}H(CO_2CH_3)_2$), 35.5 ($\underline{C}H_2$-$CH(CO_2CH_3)_2$), 31.4 ($\underline{C}H_2$), 29.7 ($\underline{C}H_2$), 28.7 ($\underline{C}H_2$-C=C), 22.6 ($\underline{C}H_2$), 22.3 ($\underline{C}H_3$-C=C); 14.4 ($\underline{C}H_3$).

MS (m/z, %) : 282 ($M^{+\bullet}$, 7), 264 (25), 121 (24), 108 (24), 107 (49), 105 (24), 93 (100), 91 (35), 79 (29), 77 (23), 55 (32).

Dimethyl 2-[2-(prop-1-en-2-yl)oct-1-en-3-yl]malonate 6.

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.25 (s, 1H, C=C$\underline{H}$H), 5.21 (s, 1H, C=C$\underline{H}$H), 4.95 (s, 1H, C=C$\underline{H}$H), 4.92 (s, 1H, C=C$\underline{H}$H), 3.73 (s, 3H, O-C$\underline{H}_3$), 3.72 (s, 3H, O-C$\underline{H}_3$), 3.66 (d, J = 9.8 Hz, 1H, C$\underline{H}(CO_2CH_3)_2$), 3.38 (dt, J = 3.7 and 9.8 Hz, 1H, CH_2-C$\underline{H}$=C), 1.90 (s, 3H, C$\underline{H}_3$-C=C), 1.2-1.5 (m, 6H, $(C\underline{H}_2)_3$), 0.89 (t, J = 6.6 Hz, 3H, C$\underline{H}_3$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 169.1 and 168.7 (2 CO), 148.8 ($\underline{C}$=CH_2), 143.2 (CH_3-$\underline{C}$=C), 113.1 (C=$\underline{C}H_2$), 112.4 (C=$\underline{C}H_2$), 57.3 ($\underline{C}H(CO_2CH_3)_2$), 52.2 (O-$\underline{C}H_3$), 40.45 ($\underline{C}$H-C=C), 33.1 ($\underline{C}H_2$), 31.9 ($\underline{C}H_2$), 29.0 ($\underline{C}H_2$), 26.2 ($\underline{C}H_2$), 21.8 ($\underline{C}H_3$-C=C).

MS (m/z, %) : 282 ($M^{+\bullet}$, 14), 152 (87), 153 (86), 135 (29), 121 (72), 109 (25), 108 (26), 107 (87), 105 (30), 95 (29), 93 (100), 91 (51), 77 (79), 55 (50).

Carbopalladation-functionalization of octa-1,2-diene with 2-bromopropene.

Palladium-catalyzed reaction. A solution of dimethyl sodiomalonate (2.6 mmol, 1.3 equiv) in THF (10 mL) was transferred *via* a canula into a solution of Pd $(PPh_3)_4$ (116 mg, 0.1 mmol) and octa-1,2-diene (220 mg, 2 mmol) in THF (8 mL). 2-Bromo-propene (484 mg, 4 mmol) was added and the reaction mixture was stirred at 65 °C for 48 h. Workup followed by flash chromatography (90:10 PE/EtOAc) gave a mixture of malonates **5** and **6** (385 mg, 68 %) which was analyzed by GLC [(E)-**5** : (Z)-**5** : **6** = 90/5/5)].

Stoichiometric reaction. A solution of $Pd(PPh_3)_4$ (475 mg, 0.5 mmol), octa-1,2-diene (56 mg, 0.5 mmol) and 2-bromopropene (67 mg, 0.55 mmol) in THF (5 mL) was heated at 45 °C for 24 h. Dimethyl sodiomalonate (0.65 mmol, 1.3 equiv) in THF (5 mL) was then added *via* a cannula and the reaction mixture was stirred at 45 °C during 24 h. Similar workup and flash chromatography afforded a mixture of malonates **5** and **6** (546 mg, 40 %) [GLC analysis : (E)-**5** : (Z)-**5** : **6** = 86/4/10].

Carbopalladation-functionalization of oct-1,2-diene in the presence of acetate anion.

As an exemple, a palladium-catalyzed version carried out with NBu_4OAc is given (Table I, entry 2) :

To a solution of $Pd(PPh_3)_4$ (87 mg, 0.075 mmol), octa-1,2-diene (165 mg, 1.5 mmol) and NBu_4OAc (1.5 g, 4.95 mmol) in THF (5 mL), we added a solution of freshly prepared dimethyl sodiomalonate (1.8 mmol) in THF (5 mL). 2-Bromopropene (20.6 μL, 1.8 mmol) was added and the reaction mixture was stirred at 40-45 °C for 48 h. Workup and flash chromatography gave a mixture of malonates **5** and **6** (276 mg, total 65 % yield) [GLC analysis : (E)-**5** : (Z)-**5** : **6** = 80/7/13].

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