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CARBOPALLADATION OF ALLENIC HYDROCARBONS.
A NEW WAY TO FUNCTIONALIZED STYRENES AND 1,3-BUTADIENES.

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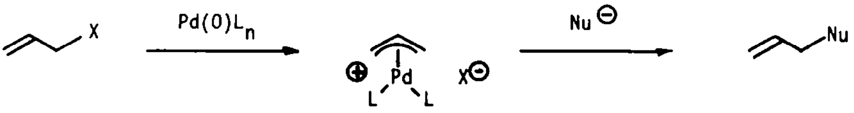
Abstract .The palladium-catalyzed coupling reaction of allenes, vinyl or aryl halides and stabilized carbanions is described : π-allyl palladium complexes are formed by addition of a vinyl or an aryl-palladium complex to an allenic hydrocarbon and trapped by the sodium enolate of diethyl malonate giving rise with good yields to β-butadienyl or β-styryl malonates. With monoalkyl allenes, the reaction is regiospecific with attack of the nucleophile on the unsubstituted carbon of the intermediate π-allyl complex and in many cases highly stereoselective with the predominant formation of the E configuration for the trisubstituted double bond of the diene. This configuration was demonstrated by ^{1}H NMR using NOE difference spectroscopy.

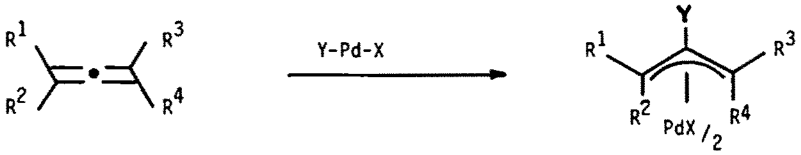
π-Allyl palladium complexes are more and more valuable intermediates in organic synthesis since the pioneering work of J.TSUJI on one hand (1) and B.M.TROST on an other hand (2)(3).

Different methods have been described for their preparation : reaction of a palladium(II) salt with an ethylenic hydrocarbon (4), metal exchange from an allylic organometallic compound (5), addition of a palladium(II) complex to a conjugated diene (6) or to a vinylcyclopropane (7). However, the more popular way remains the oxidative addition of an allylic substrate (ether, ester, epoxide, etc...) to a palladium(0)-phosphine complex since that reaction, generally followed by the attack of a nucleophile on the π-allyl complex (Scheme 1), has the main advantage of being catalytic with respect to palladium(0). Many other features have been investigated for the transformation depicted in Scheme 1 such as regioselectivity (8), stereoselectivity (9), enantioselectivity (10), chemioselectivity (11) and the possible use of an extending number of nucleophiles. For example, the use of allylic carbonates allows almost neutral conditions since nucleophilic enolates are made "in situ" by using the alcoholate liberated on formation of the palladium complex (12).



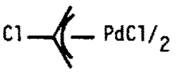
<Scheme 1>

Another method to obtain π-allyl palladium (or in general π-allyl metal) complexes consists of the addition to allenic compounds of a palladium(II) species Y-Pd-X in which Y can represent a carbon or a heteroatomic group (13, 14) (Scheme 2).



<Scheme 2>

This way was first explored in 1964 by two separate teams who described the two dimer complexes 1 and 2 formed selectively in good yields, depending on the experimental conditions, by the reaction of palladium dichloride with 1,2-propadiene (13). A few years later, the same possibility of adding palladium(II) species to an allene was also demonstrated by the description of several complexes 3 obtained from substituted allenes and π-allyl palladium complexes (14a,b) or a π-pallado-norbornene (14c).



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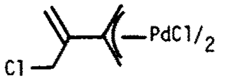

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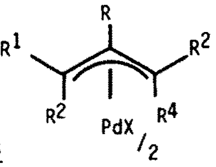

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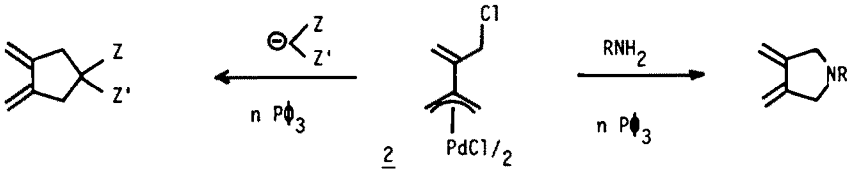
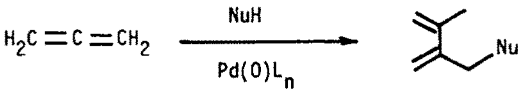
Besides these structural examples little has been done in order to use these π-allyl palladium complexes derived from allenes in synthesis. Recently, HEGEDUS et al. used the reaction of enolates and amines with 2 and obtained 1,2-dimethylenic carbo and aza five membered rings, but the interest of this work was partly overshadowed by the stoichiometric use of palladium (15) (Scheme 3).



<Scheme 3>

From this point of view, the prior work of COULSON was of interest since it showed that the reaction of amines and of the enolate of diethyl malonate with 1,2-propadiene in the presence of a catalytic amount of a palladium complex produced, with variable yields, compounds of general formula 4, probably via a metallacyclic intermediate 5 (16). Here again the palladium promoted reaction consisted of oligomerization and consequently its application in synthesis was somewhat limited.



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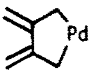

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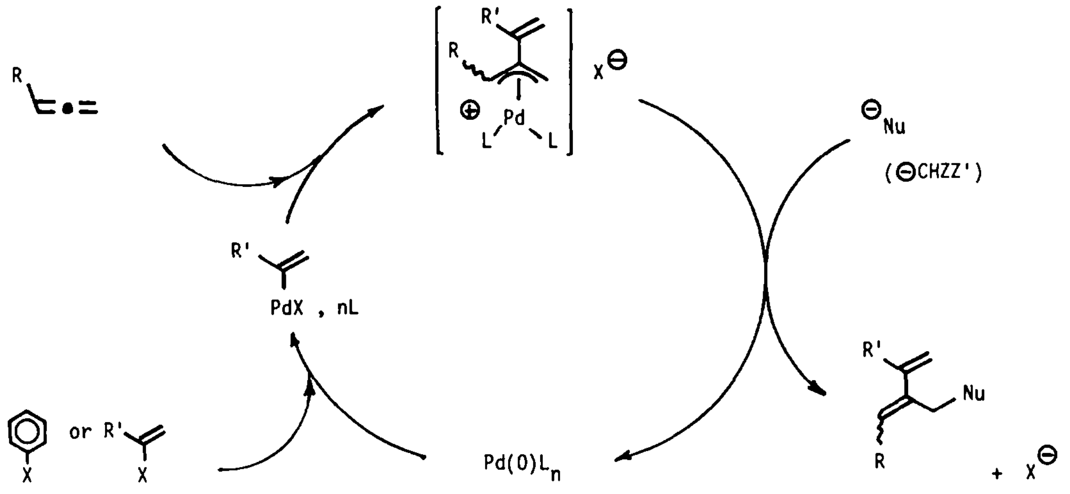
In this paper, we will described the addition of phenyl or vinyl σ-palladium species to diversely substituted allenes in order to produce regio and stereoselectively π-allyl palladium complexes able to participate in a catalytic process and lead to functionalized styryl or 1,3-dienic compounds as shown below (see ref. 17 for our preliminary communication) .



RESULTS and DISCUSSION

Reaction with 1,2-decadiene 6a .

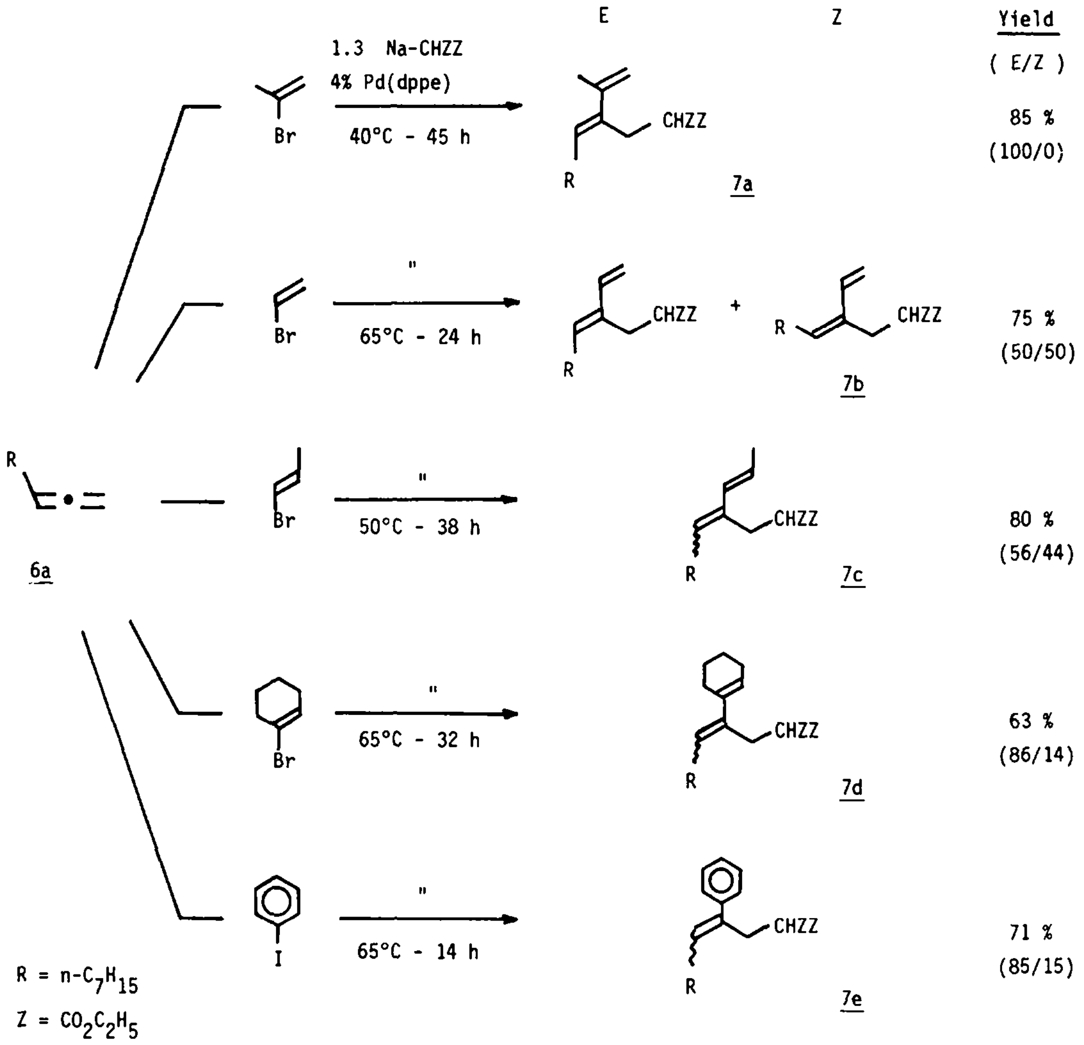
Since 1,2-propadiene is a low-boiling compound, we have chosen, for the sake of convenience, to begin our study by using 1,2-decadiene 6a easily prepared according to (18) by the reaction of n-heptyl magnesium bromide with the methyl ether of propargylic alcohol in the presence of a catalytic amount of copper bromide.

Compound 6a was reacted in THF at 40°C with 2-bromopropene (2 molar equivalents) and the sodium enolate of diethyl malonate (1.3 molar equivalent) in the presence of 4 % of tetrakis(triphenylphosphine)palladium $Pd(P\phi_3)_4$, the reaction being followed by analytical gas chromatography . A slow reaction took place, leading to a new compound . However, this reaction stopped after 24 hours and the dienic diester 7a could be isolated in a 30 % yield together with about 60 % of the starting allene 6a .

A better result was observed when the system $Pd(dba)_2 + 2P\phi_3$ was used as the catalytic system : the reaction stopped after 20 hours but was still incomplete with 30 % of remaining 6a besides 61 % of the diester 7a . Finally, the best result was obtained by using the complex Palladium(0)-bis(diphenylphosphino)ethane [Pd(dppe)] as catalyst, prepared "in situ" from bis(dibenzylideneacetone)palladium [$Pd(dba)_2$] and one equivalent of dppe . The reaction was still slow but was complete within 45 hours, giving an 85 % yield of the diester 7a .

Other conditions were also tested for the same reaction but were less attractive than those quoted above. For example, the reaction was slow and incomplete in DMF, giving only 51 % of diester 7a after 56 hours . A similar result was also observed when the catalytic system was $Pd(dba)_2$ + 2 dppe .

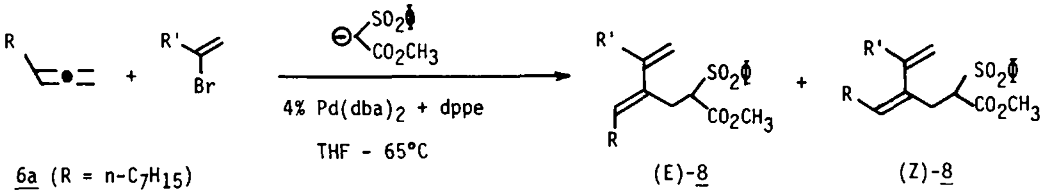
Reaction of 1,2-decadiene 6a with other vinylic bromides and with iodobenzene was studied under the best conditions previously determined (THF, 4 % of $Pd(dba)_2$ + 1 dppe, 1.3 equiv. of the sodium enolate of diethyl malonate). Slightly different temperatures were used depending on the boiling point of the unsatured halide (Scheme 4) . The reactions were monitored by gas chromatography (diester 7b , 7c) or thin layer chromatography (diester 7d , 7e) and stopped when the allene 6a was completely consumed. In the case of the gaseous vinyl bromide, the reaction had to be run in a stainless steel autoclave and its time was fixed by comparison with the other examples.



<Scheme 4> : All the reactions were performed in THF using 4% of [Pd(dba)$_2$ + 1 dppe] and the enolate of diethyl malonate Na-CHZZ (Z = COOEt).

As seen on Scheme 4 , the reaction is always regiospecific and the diester 7 obtained is formed in all cases by attack on the less substituted carbon of the intermediate π-allyl palladium complexe. On the other hand, the reaction is stereospecific in the case of 2-bromopropene, highly stereoselective with 1-bromocyclohexene and iodobenzene but the stereoselectivity is completely lost with (E)-1-bromopropene and vinylbromide. Generally, both isomers were separated by flash chromatography (7b) or preparative HPLC (7c , 7e). In the case of 7d , the separation of the isomers was impossible and the percentages were determined by ^1H NMR on the signal of the acyclic vinylic hydrogen. The determination of the configuration of the trisubstituted double bond was made in a few cases by using Nuclear Overhauser Effect difference spectroscopy (19) and in the other examples, by ^{13}C NMR spectroscopy (see below).

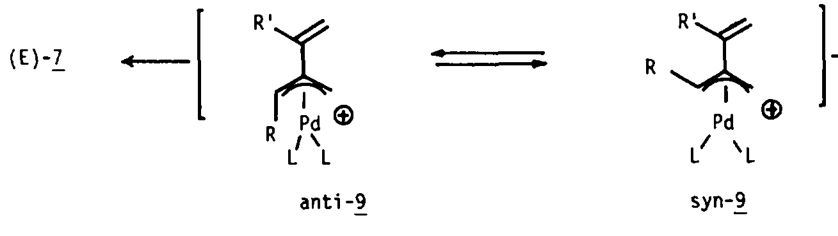
The stereochemistry of the process is not only dependent on the vinylic halide but also on the nature of the entering nucleophile. Thus, the reaction of the enolate of methyl α-phenylsulfonyl acetate with the π-allyl palladium intermediate formed from 2-bromopropene (Scheme 5 - R'= CH_3) is less stereoselective than the one with diethyl malonate since it leads to a E/Z = 80/20 mixture of the stereoisomers of the dienic diester 8a . Furthermore the reverse stereoselectivity (8b , E/Z = 30/70) is observed in the case of the reaction of the same enolate with the π-allyl complex formed from vinylbromide (scheme 5 - R'= H). In both cases, it was not possible to separate the isomers and their ratio were determined by using ^{1}H NMR spectroscopy (8b) or ^{13}C NMR spectroscopy (8a).



48 h	71%	8a (R'= CH_3)	E/Z = 80/20
38 h	57%	8b (R'= H)	E/Z = 30/70

<Scheme 5>

The stereoselectivity of the reaction seems mainly related to the steric hindrance of the incoming unsaturated (arylic or vinylic) halide and can be discussed in term of the relative stabilities of the intermediate syn or anti π-allyl complexes 9 which are generated from the insertion of the allenic pattern in the sp^2 -carbon - palladium bond (Scheme 6). The complex anti- 9 would be the kinetically produced complex corresponding to an anti entrance of the σ-vinylic palladium complex referred to the alkyl substituent of the allene, as already demonstrated for Grignard reagents or cuprates (20). This would explain the highly stereoselective formation of the styryl or 1,3-dienic compounds (E)- 7 when R' is a large group (R' = CH_3). Smaller steric interactions between the n-heptyl group and a less bulky unsaturated group (e.g. vinyl group, R' = H) would favor the isomerisation to the complex syn- 9 : a smaller or a reverse stereoselectivity would then be observed (compare 7a and 7b or 8a and 8b).

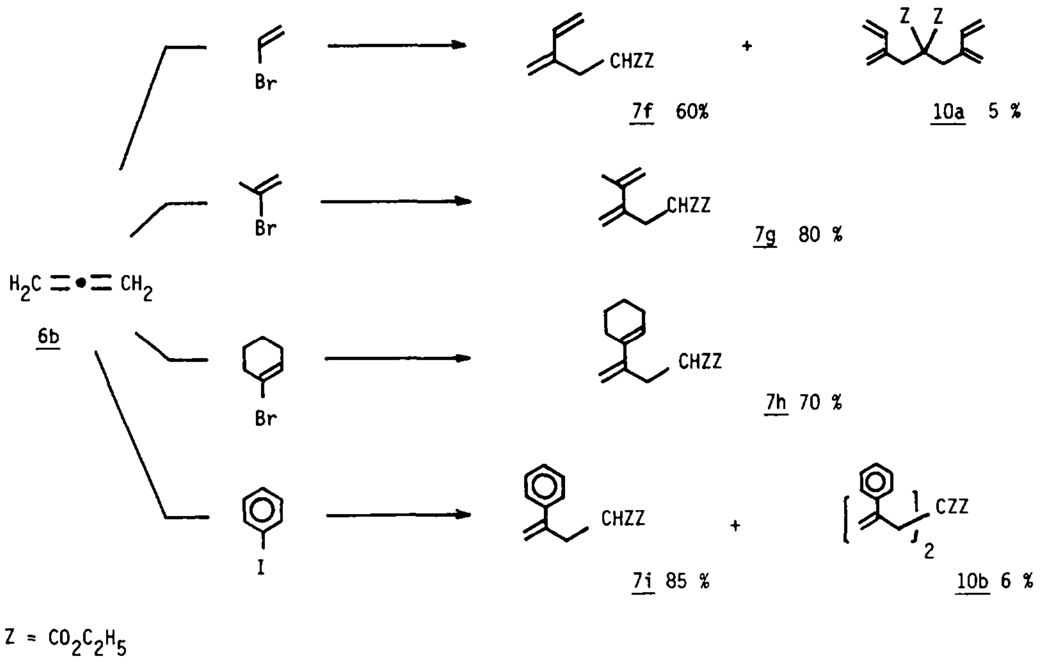


<Scheme 6>

Reactions with 1,2-propadiene .

Referred to the above-mentioned results, 1,2-propadiene 6b was reacted with different vinylic bromides and iodobenzene in the presence of the sodium enolate of diethyl malonate (1,3 equiv.) and 2 % of the catalytic system $Pd(dba)_2$ + dppe. All the reactions described in Scheme 7 were performed at 65° C in a stainless steel autoclave with THF as solvent.

In all cases, the functionalized 1,3-diene 7 was obtained in fairly good yields after purification by distillation or by flash chromatography. In two cases it was possible to isolate also some dialkylation product 10 as a minor compound (about 5 %).



<Scheme 7>

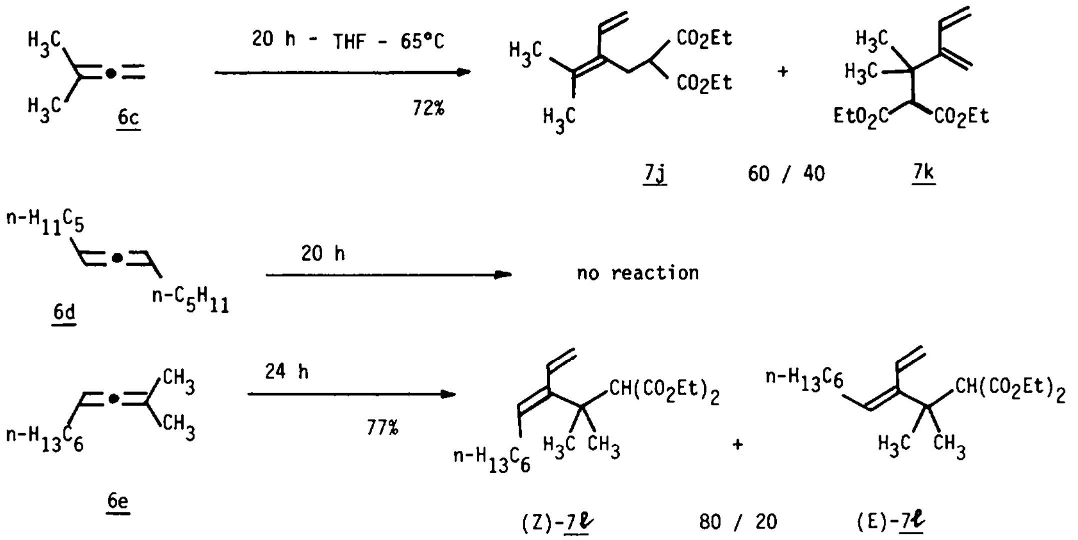
Reactions with other allenes .

Three other allenes 6c , 6d and 6e were selected in order to test the scope and limitations of the described reaction. The non-commercial 6,7-tridecadiene 6d and 2-methyl-2,3-decadiene 6e were easily obtained according to (21) by the reaction of an alkylcopper derivative (RMgX + 1 mol. equiv. of CuBr ; THF ; -30°C) with the tosylates of respectively 1-octyne-3-ol and 3-methyl-1-butyne-3-ol.

The reactions with these allenes were run using vinyl bromide, the sodium enolate of diethyl malonate (1,3 mol. equiv.) and 3 % of the Pd(dppe) catalyst. They were performed in a stainless steel autoclave at 65°C using THF as solvent. The results are given in Scheme 8.

No regiospecificity was observed in the case of 1,1-dimethylallene 6c , both electrophilic poles (primary and tertiary) of the intermediate π-allyl palladium complex being attacked in almost the same extent by the incoming nucleophile as it was previously described in the case of π-allyl complexes unsubstituted on the central carbon atom (7b). On the contrary, the reaction is again regiospecific in the case of 6e with essentially only attack on the tertiary pole and no reaction on the secondary one. This is in accord with the unreactivity of allene 6d under those conditions.

However, the reaction involving 6e is slow due to the steric hindrance of the intermediate π-allyl palladium complex. After 24 hours, only 38% of the starting allene had been consumed and the 77% yield in that case refers to the conversion of 6e . As shown in the Scheme 8, the reaction is stereoselective and leads to the isomer (Z)-7l as the major isomer [Z:E = 80:20 , as established by ^{13}C NMR. According to nomenclature rules, this major isomer must be given a (Z)-configuration even if it presents the same trans stereorelationship between the vinyl and the alkyl groups as the one in compounds (E)-7a-e].

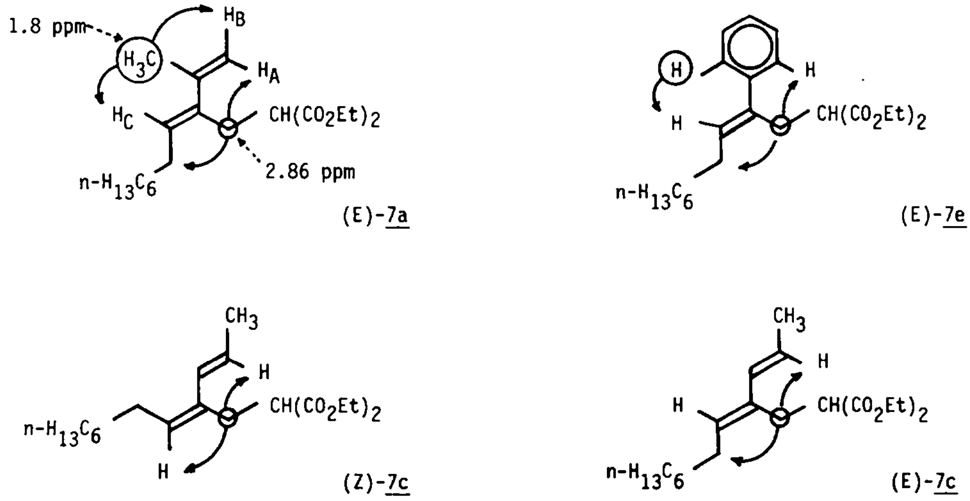


<Scheme 8>

Determination of the configuration of the dienes 7 .

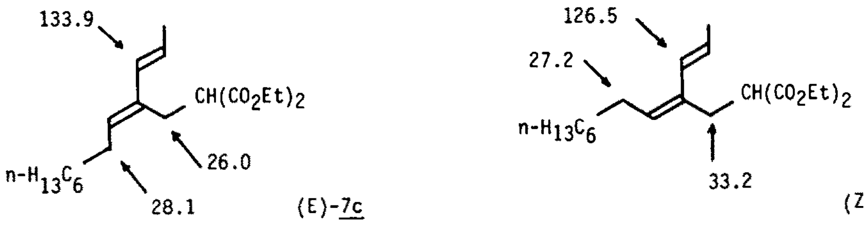
As previously mentioned, the determination of configuration was mainly done by differential Nuclear Overhauser Effect (NOE) [^1H NMR spectroscopy (200 MHz)] on the only isolated isomer of 7a , on both isomers of 7c isolated in pure form by preparative HPLC, and on the more abundant E isomer of 7e . In the case of 7a , the irradiation of the methylene group at 2.86 ppm which is part of the substituent bearing the malonate moiety has an influence only on the signal of the methylene of the heptyl group (2.05ppm) and on that of the olefinic proton H_A (4.86ppm). On an other hand, the irradiation of the olefinic methyl group at 1.8 ppm gives an effect only on the vinylic protons H_B (4.05 ppm) and H_C (5.56 ppm) (Scheme 9). These effects prove undoubtly that the isolated diene 7a has the E configuration of the trisubstituted double bond and provide good evidence for an s-trans conformation of the butadienyl moiety.

The same effects were also noticeable in the case of the major isomer of the functionalized styrene 7e and on both isomers of diene 7c , as shown in Scheme 9, where the arrows indicate the differential NOE which were only observed by irradiating the encircled proton(s).



<Scheme 9>

The same conclusions concerning the configuration of the trisubstituted double bond can be also deduced from the chemical shifts in ^{13}C NMR spectroscopy. The comparison of these parameters for the three α-carbon atoms of this double bond in both isomers shows a neat shielding due to reciprocal cis-γ-effect (22). This result, that will be detailed in the future in the case of differently substituted 1,3-butadienes (23) is exemplified in Scheme 10 where the shifts are given in ppm downfield from tetramethylsilane.

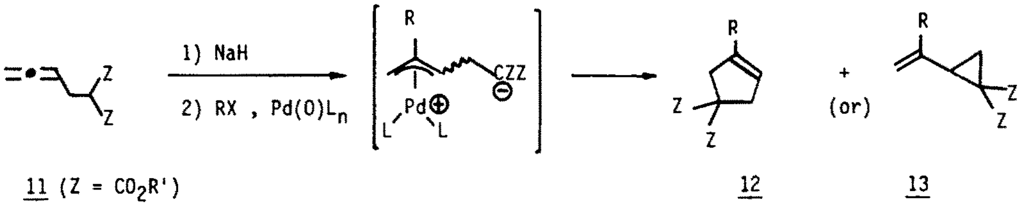


<Scheme 10>

CONCLUSION.

The above mentioned results show that the carbopalladation of allenic hydrocarbons by vinyl or aryl palladium σ-complexes in the presence of a malonate type nucleophile permits, by a catalytic process, to create simultaneously two carbon-carbon bonds. This regio and stereoselective reaction leads to useful products that could be converted to valuable synthons by Diels-Alder annulation.

Our own work in this field was very recently complemented by other groups who used different external (24) or internal (25) nucleophiles or different entering palladium complex (26). We have also described (27) the same reaction in the case of the β-allenylmalonate 11 , easily obtained from the palladium-promoted substitution of α-allenic ester (20a), where the intramolecular attack on the π-allyl palladium complex by the enolate gives rise to cyclopentene 12 or (and) vinylcyclopropane 13 (Scheme 11) depending on the nature of the R group.



<Scheme 11>

EXPERIMENTAL SECTION

General methods . Ether, tetrahydrofuran (THF) and dimethylformamid (DMF) were distilled from CaH_2, sodium benzophenone ketyl and P_2O_5 respectively. Petroleum ether (P.E) used for chromatography was distilled from P_2O_5 (b.p 40-55°C).

Reagents and solutions were transferred via syringes and stainless steel cannulae. Reactions were conducted under positive pressures of argon. Workup included drying of the ether solution of the crude products over anhydrous magnesium sulfate and removal of solvents on a rotatory evaporator under partial water aspirator vacuum.

Column chromatography was carried out with silica gel 60 (from Merck, 70-230 Mesh). "Flash Chromatography" using silica gel 60 (230-400 mesh) refers to the procedure of W.C.STILL and all (28). High-performance liquid chromatography (HPLC) was done with a Waters model 6000A liquid chromatograph

(differential refractometer). Capillary GLC analysis (OV101 or FFAP columns) were performed on a GIRDEL-DELSI 330 gas-chromatograph equipped with a flame ionization detector (250°C) and nitrogen carrier gas. Preparative GLC were performed on a 1700 Varian Aerograph (Helium carrier gas).
Infrared (IR) spectra were determined with a Perkin-Elmer 298 recording spectrophotometer. Only the most prominent or diagnostic peaks are reported .
^{1}H NMR spectra were recorded on the following spectrometers : Varian EM360 (60MHz) and Bruker 80CW (80MHz) for routine spectra, Bruker 200WP and Cameca 350, FT instruments operating at 200 and 350 MHz. ^{13}C NMR spectra were measured at 50.1MHz or 88 MHz. Chemical shifts are expressed in ppm downfield from tetramethylsilane. Significant ^{1}H MR data are tabulated in the order : multiplicity (s, singlet ; d, doublet ; t, triplet ; q, quartet ; m, multiplet), coupling constant(s) in hertz, number of protons.
Mass Spectra (MS), m/z (relative intensity) were obtained from a Varian-Mat CH5 at 70eV.
Elemental analysis of 7a,f,g,h,i,k were performed by the "Service Central d'Analyse du CNRS". All new homologous compounds 7 and 8 were homogeneous after flash chromatography purification ; their ^{1}H NMR and ^{13}C NMR spectra did not show the presence of any impurity (<5%).

Materials
1,2-propadiene and 1,1-dimethylpropadiene are commercially available from Matheson and Aldrich Chemical Co. respectively . 1,2-decadiene 6a (18) and 1-bromocyclohexene (29) were prepared according to the literature procedures. (E)-1-bromo-1-propene was purified (distillation through a spinning-band column, b.p 62-63°C/760mm) from a commercial E-Z mixture. $Pd(dba)_2$ is commercial from Janssen Chimica.

2-Methyl-2,3-decadiene 6e .

A solution (THF, 110 mL) of 0.11 mol of the instable mesylate of commercial 2-methyl-3-butyn-2-ol is prepared at -60°C from 0.11 mol of this alcohol and 0.12 mol of methanesulfonyl chloride (21). 0.11 mol of n-hexylmagnesiocuprate, prepared at -50°C, is transferred at this temperature through a cannula to the solution of the mesylate maintained at -50°C. The temperature of the mixture is then raised to 20°C over 30 min (21). Workup and distillation gave 2g (13% yield) of 1-bromo-2-methyl-1,2-butadiene [b.p 48-54°C (25 mm) ; ^{1}H NMR (60MHz, CCl_4) : 2.75 (d, J=3Hz, 6H) ; 5.7 (m, 1H)] and 10.31g (61% yield) of allene 6e , b.p 76-80°C (20 mm).
IR (film) : 2945, 2920, 2840, 1910, 1460, 785 cm^{-1}.
^{1}H NMR (CCl_4 , 60MHz): 0.9 (t, J=5.5Hz, 3H); 1.3 (m, 8H); 1.6 (d, J=2.5Hz, 6H); 1.8 (m, 2H) ; 4.8 (m, 1H).

General procedures for the preparation of functionalized styrenes and dienes 7 .

Procedure A (scale relative to the allenic hydrocarbon 6) .

A solution of diethyl sodiomalonate was first prepared by adding at 0°C 416 mg (2.6 mmol) of diethyl malonate to 130 mg of a 50% dispersion of sodium hydride (2.7 mmol, washed free of mineral oil with THF) in 10 mL of dry THF and then stirring for 20-30 min at 20°C. This solution wad added via a transfer needle in a solution of THF (10 mL) containing 46 mg (0.08 mmol, 4% molar referred to the allene 6) of $Pd(dba)_2$, 32 mg (0.08 mmol) of 1,2-bis(diphenylphosphino)ethane [dppe], the allenic hydrocarbon 6 (2 mmol) and the unsaturated organic halide (2 or 3 mmol). The reaction mixture is stirred (24-50 h) at 40-65°C according to the nature of the halide (see Schemes 4 and 7) ; it is then diluted with some ether, poured into a NH_4Cl aqueous solution and extracted with ether (∼2x60 mL). The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. Removal of solvents in vacuo gave an oil which was filtrated at once on a short column of silica gel (petroleum ether/ether : 95/5) before analysis (TLC, GLC, IR). Purification of malonate 7 was then carried out by distillation, silica gel or GL chromatography.

Procedure B , used with low boiling compounds, 1,2-propadiene 6b (the scale is then relative to the unsaturated halide) or vinyl bromide.

$Pd(dba)_2$ (115 mg, 0.2 mmol) and 1,2-bis(diphenylphosphino)ethane (80 mg, 0.2 mmol) were introduced in a 125 mL stainless steel autoclave which is then closed with a rubber septum, purged with argon and cooled at -78°C. Anhydrous THF (25 mL) and liquid 1,2-propadiene 6b (20 mmol, 0.45 mL condensed at -78°C) are transferred into the autoclave. A solution of 13 mmol of diethyl sodiomalonate in THF (15 mL) prepared as above is added via a transfert needle, before the introduction of the unsaturated organic halide (10 mmol). The autoclave is then closed and heated for 24h. Workup and purification were then carried out as in procedure A .

Diethyl 2-[(E)-2-(isopropenyl)-2-decenyl] propanedioate 7a .

Procedure A (2 mmol scale ; 40°C ; 45 h). Flash chromatography (90:10 P.E/AcOEt) of the crude product gave 576 mg (85% yield) of the diester 7a .
IR (neat) : 3080, 3020, 1740, 1630, 1605, 1230, 890 cm^{-1}.
^{1}H NMR ($CDCl_3$, 200 MHz) : 0.81 (t, J=6.6Hz, 3H) ; 1.17 (t, J=7.1, 6H) ; 1.21 (m, 10H) ; 1.80 (s, 3H) ; 2.10 (q, J=7.3Hz, 2H) ; 2.86 (d, J=7.3Hz, 2H) ; 3.47 (t, J=7.3Hz, 1H) ; 4.08 (q, J=7.1Hz, 4H) ; 4.85 (s, 1H) ; 4.87 (s, 1H) ; 5.56 (t, J=7.3Hz, 1H).
MS (m/z) : 338 ($M^{+\bullet}$, 50), 320 (60), 293 (36) ; 264 (40), 218 (16), 191 (25), 178 (45), 160 (42), 133 (33), 121 (30), 107 (52), 93 (100), 79 (32), 55 (40).

^{13}C NMR (CDCl$_3$, 50.1 MHz) : 13.9, 13.9, 21.3, 22.5, 26.6, 28.3, 29.1, 29.3, 29.6, 31.7, 51.0, 61.0, 111.2, 131.1, 135.7, 142.9, 169.1 .
Anal.Calcd for C$_{20}$H$_{34}$O$_4$: C,70.97 ; H,10.12 . Found : C, 71.14 ; H, 9.87 .

Diethyl 2-(2-vinyl-2-decenyl) propanedioate 7b .

Procedure A (4 mmol scale ; 65°C ; 24 h). Flash Chromatography (90:10 P.E/AcOEt) of the crude product gave 976 mg (75 % yield) of a 1:1 mixture of (E) and (Z)-diesters 7b .
GLC (OV 101, 25m, 220°C) : E:Z = 50:50

IR (neat) (E + Z mixture) : 3080, 1740, 1670, 1645, 1595, 1230, 910 cm^{-1}.

MS (m/z) of the E+Z mixture : 324 (M$^{+\cdot}$, 50), 306 (20), 279 (41), 250 (26), 233 (17), 204 (37), 177 (31), 164 (100), 160 (51), 133 (38), 107 (57), 83 (61), 79 (87), 55 (61), 43 (78).
Pure (E) and (Z)- isomers were obtained through a second flash chromatography of 500 mg of this (E + Z) mixture on 100 g of silica gel.

Malonate (E)- 7b .

^{1}H NMR (CDCl$_3$, 350 MHz) : 0.87 (t, J=7Hz, 3H) ; 1.25 (t, J=7Hz, 6H) ; 1.28 (br.s, 10H) ; 2.12 (q, J=7Hz, 2H) ; 2.88 (d, J=7.4Hz, 2H) ; 3.54 (t, J=7.4Hz, 1H) ; 4.16 (q, J=7Hz, 4H) ; 4.95 (d, J=11.2Hz, 1H) ; 5.08 (d, J=17.5Hz, 1H) ; 5.56 (t, J=7Hz, 1H) ; 6.23 (dd, J=11.2Hz and 17.5Hz, 1H).

^{13}C NMR (50.1 MHz) : 14.1, 14.1, 22.7, 25.4, 28.3, 29.2, 29.2, 29.6, 31.9, 50.9, 61.3, 110.8, 133.8, 136.0, 139.2, 168.8 .

Malonate (Z)- 7b .

^{1}H NMR (CDCl$_3$, 350 MHz) : 0.88 (t, J=7Hz, 3H) ; 1.24 (t, J=7Hz, 6H) ; 1.26 (br.s, 10H) ; 2.12 (q, J=7Hz, 2H) ; 2.81 (d, J=7.4Hz, 2H) ; 3.60 (t, J=7.4Hz, 1H) ; 4.17 (q, J=7Hz, 4H) ; 5.13 (d, J=11.2Hz, 1H) ; 5.24 (d, J=17.5Hz, 1H) ; 5.46 (t, J=7.7Hz, 1H) ; 6.62 (dd, J=11.2Hz and J=17.5Hz, 1H).

^{13}C NMR (CDCl$_3$, 50.1 MHz): 14.1, 14.1, 22.7, 27.5, 29.2, 29.2, 29.7, 31.9, 32.6, 51.4, 61.3, 113.5, 132.1, 132.6, 133.7, 169.3.

Diethyl 2-[2-(1'-propenyl)-2-decenyl] propanedioate 7c .

Procedure A (2 mmol scale ; 50°C ; 38 h). Flash chromatography (90:10 P.E/AcOEt) of the filtered product gave 541 mg (80 % yield) of a 64:46 mixture of the (E) and (Z)-diesters 7c .
GLC (OV 101, 25m, 220°C) : E:Z = 64:46

IR (neat) (E + Z mixture) : 3010, 1740, 1670, 1575, 1230, 965, 785 cm^{-1}.

MS (m/z) of the E+Z mixture : 338 (M$^{+\cdot}$, 22), 243 (24), 240 (100), 124 (38), 178 (57), 167 (33), 149 (28), 121 (49), 107 (49), 95 (71), 93 (98), 71 (39), 57 (55), 55 (59).
These stereoisomers were separated through a C$_{18}$ inverted phase HPLC (MeOH/H$_2$O = 85/15).

Malonate (E)- 7c .

^{1}H NMR (CDCl$_3$, 200 MHz) : 0.83 (t, J=6.8Hz, 3H) ; 1.23 (t, J=7.1Hz, 6H) ; 1.24 (m, 10H) ; 1.72 (d, J=6.6Hz, 3H) ; 2.06 (q, J=7Hz, 2H) ; 2.83 (d, J=7.6Hz, 2H) ; 3.51 (t, J=7.6Hz, 1H) ; 4.14 (q, J=7.1Hz, 4H) ; 5.40 (t, J=7Hz, 1H) ; 5.54 (qd, J=6.6 and J=16Hz, 1H) ; 5.92 (d, J=16Hz, 1H).

^{13}C NMR (CDCl$_3$, 50.1 MHz) : 14.0, 14.0, 18.3, 22.6, 26.0, 28.1, 29.2, 29.3, 29.7, 31.8, 51.2, 61.3,122.2, 133.3, 133.5, 133.9, 169.3 .

Malonate (Z)- 7c .

^{1}H NMR (CDCl$_3$, 200 MHz) : 0.83 (t, J=6.6Hz, 3H) ; 1.20 (t, J=7.2Hz, 6H) ; 1.21 (m, 10H) ; 1.76 (d, J=6.6Hz, 3H) ; 2.05 (q, J=7.5Hz, 2H) ; 2.73 (d, J=7.6Hz, 2H) ; 3.53 (t, J=7.6Hz, 1H) ; 4.12 (q, J=7.2Hz, 4H) ; 5.25 (t, J=7.5Hz, 1H) ; 5.67 (qd, J=6.6Hz and J=16Hz, 1H) ; 6.24 (d, J=16Hz, 1H).

^{13}C NMR (CDCl$_3$, 50.1 MHz) : 14.0, 14.0, 18.6, 22.6, 27.2, 29.1, 29.1, 29.6, 31.7, 33.2, 51.4, 61.1, 124.8, 126.5, 130.7, 131.9, 169.1 .

Diethyl 2-[2-(1'-cyclohexenyl)-2-decenyl] propanedioate 7d .

Procedure A (2 mmol scale ; 65°C ; 32 h). Flash chromatography (90:10 P.E/AcOEt) of the crude product gave 473 mg (62 % yield) of a 85:15 mixture (ratio based on NMR integration of vinylic protons at 5.70 and 5.36 ppm) of the (E) and (Z)-diesters 7d .

IR (E + Z mixture) : 3020, 1740, 1640, 1600, 1230 cm^{1}.

^{1}H NMR (CDCl$_3$, 350 MHz) of (E)- 7d : 0.88 (t, J=7Hz, 3H) ; 1.24 (t, J=7Hz, 6H) ; 1.28 (m, 10H) ; 1.5-1.7 (m, 4H) ; 2.10 (m, 6H) ; 2.88 (d, J=7Hz, 2H) ; 3.49 (t, J=7Hz, 1H) ; 4.15 (q, J=7Hz, 4H) ; 5.48 (t, J=7.4Hz, 1H) ; 5.70 (br.s, 1H). [(Z)-7d isomer : vinylic signals at 5.16 ppm (t, J=7Hz, 1H) and 5.36 ppm (s, 1H)].

MS (m/z) (E + Z mixture) : 378(M$^{+\cdot}$, 3), 218 (10), 147 (19), 133 (100), 105 (14), 95 (47), 91 (22), 79 (13), 75 (20), 73 (17), 55 (16), 43 (30).

^{13}C NMR (CDCl$_3$, 50.1 MHz) of (E)-7d : 13.9, 13.9, 22.1, 22.5, 22.9, 25.6, 26.4, 26.6, 28.1, 29.0, 29.1, 29.2, 31.7, 50.1, 60.9, 122.9, 127.8, 136.2, 136.5, 169.2 .

Diethyl 2-(2-phenyl-2-decenyl) propanedioate 7e .

Procedure A (2 mmol scale ; 65°C ; 14 h). Flash chromatography (90:10 P.E/AcOEt) of the filtrered product gave 532 mg (71 % yield) of a 85 : 15 (ratio based on NMR integration of vinylic protons at 5.57 and 5.41 ppm) mixture of (E) and (Z)- diesters 7e respectively. These stereoisomers were separated by C_{18} inverted phase HPLC using 15 % aqueous MeOH as eluent system.

IR (E + Z mixture) : 3070, 3040, 3010, 1740, 1590, 1570, 1230, 760, 700 cm^{-1}.

MS (m/z) (E + Z mixture) : 374($M^{+\cdot}$, 30), 356 (13), 328 (15), 276 (7), 214 (100), 173 (15), 160 (62), 143 (62), 129 (64), 71 (17), 53 (32), 40 (41).

Malonate (E)- 7e .

^1H NMR ($CDCl_3$, 200 MHz) : 0.77 (t, J=6.6Hz, 3H) ; 1.08 (t, J=7Hz, 6H) ; 1.17 (m, 10H) ; 2.10 (q, J=7Hz, 2H) ; 3.03 (B_2 part of an AB_2 system, J=19Hz, 2H) ; 3.21 (A part of an AB_2 system, J=19Hz, 2H) ; 3.97 (q, J=7Hz, 4H) ; 5.57 (t, J=7.2Hz, 1H) ; 7.16 (s, 5H).

^{13}C NMR ($CDCl_3$, 50.1 MHz) : 13.9, 14.0, 22.6, 28.5, 28.8, 29.2, 29.3, 29.7, 31.8, 50.7, 61.2, 126.7, 126.9, 128.2, 132.5, 135.9, 142.0, 169.1 .

Malonate (Z)-7e .

^1H NMR ($CDCl_3$, 200 MHz) : 0.77 (t, J=6.6Hz, 3H) ; 1.08 (t, J=7Hz, 6H) ; 1.27 (m, 10H) ; 1.78 (q, J=6.8Hz, 2H); 2.8 (d, J=7.6Hz, 2H); 3.5 (t, J=7.6Hz, 1H); 4.1 (q, J=7Hz, 4H); 5.41 (t, J=6.8Hz, 1H); 7.3 (s, 5H).

Diethyl 2-(2-methyliden-3-butenyl) propanedioate 7f .

Procedure B (20 mmol scale ; 65°C ; 19h). Filtration of the crude product gave 4.35 g. Flash chromatography (90:10 P.E/AcOET) of 500 mg of this filtered material gave 312 mg of pure diester 7f (60% yield) and 65 mg of the dialkylated malonate 10a . The remaining filtered product (3.85 mg) was distillated to give 1g of pure 7f (b.p 55-60°C/0.03mm).

Malonate 7f .

IR : 3080, 3040, 1740, 1635, 1600, 1580, 1230, 910 cm^{-1} .

^1H NMR ($CDCl_3$, 80MHz) : 1.27 (t, J=7Hz, 6H) ; 2.86 (d, J=7.4Hz, 2H) ; 3,63 (t, J=7.4Hz, 1H) ; 4.20 (q, J=7Hz, 4H) ; 5.10 (s, 2H) ; 5.12 (d, J=11Hz, 1H) ; 5.3 (d, J=17Hz, 1H) ; 6.4 (dd, J=11Hz and J=17Hz, 1H).

MS (m/z) : 226 ($M^{+\cdot}$, 15) , 181 (7), 160 (15), 133 (58), 115 (100), 88 (33), 79 (32), 43 (73).

Anal.calcd for $C_{12}H_{18}O_4$: C, 63.69 ; H, 8.02 . Found : C, 63.49 ; H, 8.28 .

Diethyl 2,2-bis(2-methylidene-3-butenyl) propanedioate 10a .

IR : 3080, 3040, 1735, 1630, 1600, 1470, 1230, 910 cm-1

^1H NMR ($CDCl_3$, 80MHz) : 1.28 (t, J=7Hz, 6H) ; 2.95 (s, 4H) ; 4.2 (q, J=7Hz, 4H) ; 4.93 (s, 2H) ; 5.05 (s, 2H) ; 5.12 (d, J=11Hz, 2H) ; 5.28 (d, J=18Hz, 2H) ; 6.31 (dd, J=11 and J=18Hz, 2H).

Diethyl 2-(2-methyliden-3-methyl-3-butenyl) propanedioate 7g .

Procedure B (20 mmol scale ; 65°C ; 20h). Flash chromatography (90:10 P.E/AcOEt) of the crude product gavec 1.92g (80 % yield) of diester 7g (b.p 70°C / 0.03 mm).

IR (neat) : 3090, 3050, 1740, 1630, 1600, 1580, 1230, 900 cm^{-1}.

^1H NMR ($CDCl_3$, 350 MHz) : 1.26 (t, J=7Hz, 6H) ; 1.90 (s, 3H) ; 2.91 (d, J=7.7Hz, 2H) ; 3.62 (t, J=7.7Hz, 1H) ; 4.19 (q, J=7.1Hz, 4H) ; 5.02 (s, 2H) ; 5.09 (s, 1H) ; 5.13 (s, 1H).

MS (m/z) : 240 ($M^{+\cdot}$, 27) ; 195(25) ; 166(51) ; 149(31) ; 139(13) ; 121(45) ; 93(100) ; 79(31) ; 77(23).

^{13}C NMR ($CDCl_3$,50.1 MHz) : 14.1, 21.2, 32.9, 51.4, 61.4, 113.2, 114.6, 141.7, 144.1, 169.2.

Anal.Calcd for $C_{13}H_{20}O_4$: C, 64.98 ; H, 8.89 . Found : C, 65.21 ; H, 8.41 .

Diethyl 2-[2-(1'-cyclohexenyl)-2-propenyl] propanedioate 7h .

Procedure B (10 mmol scale ; 65°C ; 17h). Flash chromatography (90:10 P.E/AcOEt) of the filtered product gave 1.97 g (70% yield) of diester 7h (b.p 105°C/0.03 mm).

IR (neat) : 3080, 3020, 1740, 1630, 1600, 1230, 900 cm^{-1}.

^1H NMR ($CDCl_3$, 350 MHz) : 1.26 (t, J=7.2Hz, 6H) ; 1.5-1.7 (m, 4H) ; 2.14 (br.s, 4H) ; 2.88 (d, J=7.5Hz, 2H) ; 3.58 (t, J=7.5Hz, 1H) ; 4.18 (q, 7.2Hz, 4H) ; 4.86 (s, 1H) ; 5.0 (s, 1H), 5.89 (s, 1H).

^{13}C NMR (88MHz) : 14.0, 22.1, 22.9, 25.8, 26.2, 32.3, 51.7, 61.1, 111.0, 124.6, 135.2, 145.2, 169.2.

MS (m/z) : 280 ($M^{+\cdot}$, 13), 240 (23), 206 (27), 166 (100), 161 (45), 133 (39), 115 (29), 91 (43), 81 (39).

Anal.Calcd for $C_{16}H_{24}O_4$: C, 68.54 ; H, 8,60 . Found : C, 68.26 ; H, 8.43 .

Diethyl 2-(2-phenyl-2-propenyl) propanedioate 7i .

Procedure B (20 mmol scale ; 65°C ; 17h). Filtration through 20 g silica gel gave 6.7 g of filtered product. Flash chromatography (90:10 P.E/AcOEt) of 600 mg of this filtered material afforded 405 mg

(85% yield) of diester 7i and 87 mg (6% yield) of diester 10b . Distillation of the remaining 6.1g gave 4.52 g (82% yield) of pure diester 7i (b.p 110°C / 0.02 mm).

IR (film) : 3030, 3040, 3010, 1735, 1590, 1570, 1230, 760, 700 cm^{-1}.

^{1}H NMR (CDCl$_3$, 350 MHz) : 1.24 (t, J=7Hz, 6H) ; 3.12 (d, J=7.6Hz, 2H) ; 3.49 (t, J=7.6Hz, 1H) ; 4.16 (q, J=7Hz, 4H) ; 5.14 (s, 1H) ; 5.33 (s, 1H) ; 7.32 (m, 5H).

MS (m/z) : 276 (M$^{+\cdot}$, 25), 203 (5), 185 (12), 159 (2), 157 (25), 129 (100).
Anal.Calcd for $C_{16}H_{20}O_4$: C, 69.54 ; H, 7.29 . Found : C, 69.30 ; H, 7.32 .

Diethyl 2,2-bis(2-phenyl-2-propenyl) propanedioate 10b .

IR : 3080, 3040, 3010, 1730, 1590, 1570, 1230, 760, 700 cm^{-1}.

^{1}H NMR(CDCl$_3$, 80MHz) : 0.96 (t, J=7Hz, 6H) ; 3.0 (s, 4H) ; 3.45 (q, J=7Hz, 4H) ; 5.0 (s,2H) ; 5.1 (s, 2H); 7.2 (m, 10H).

Malonates 7j and 7k . (Reaction of allene 6e with vinyl bromide).

Procedure B (6.5 mmol scale ; 65°C ; 24h). Flash chromatography (90:10 P.E/AcOEt) gave 1.19 g (72 % yield) of a 60:40 (GLC ratio) mixture of malonates 7j and 7k respectively. These one were separated by preparative GLC (5% SE 30, 200°C).

Malonate 7j .

IR (neat) : 3080, 1740, 1680, 1630, 1600, 1230, 900 cm^{-1}.

^{1}H NMR (CDCl$_3$, 350 MHz) : 1.25 (t, J=7Hz, 6H) ; 1.81 (br.s, 6H) ; 2.94 (d, J=7.4Hz, 2H) ; 3.55 (t, J=7.4Hz, 1H) ; 4.18 (q, J=7Hz, 4H) ; 5.02 (d, J_{cis} = 11.2Hz, 1H) ; 5.10 (d, J_{trans} = 17.5Hz, 1H) ; 6.69 (dd, J_{cis} = 11.2Hz and J_{trans} = 17.5Hz, 1H).

^{13}C NMR (CDCl$_3$, 88 MHz) : 14.6, 14.6,14.6, 26.8, 50.9, 61.2, 111.9, 127.6, 133.9, 134.6, 169.5 .

MS (m/z) : 254 (M$^{+\cdot}$,45), 209(18), 181(26), 163(36), 160(28), 135(15), 107(33), 95 (100), 79 (36), 67(31), 55(26).

Malonate 7k .

IR (neat) : 3080, 1760, 1735, 1680, 1630, 1610, 1150, 925, 860 cm^{-1}.

^{1}H NMR (CDCl$_3$, 350 MHz) : 1.24 (t, J=7Hz, 6H) ; 1.33 (s, 6H) ; 3.6 (s, 1H) ; 4.14 (q, J=7Hz, 4H) ; 4.90 (d, J_{gem}=0.7Hz, 1H) ; 5.07 (dd, J_{cis}=10.5Hz and J_{gem}=2.1Hz, 1H) ; 5.16 (dd, ^5J=0.8Hz and J_{gem}=0.7Hz, 1H); 5.38 (dd, J_{trans}=16.8Hz and J_{gem}=2.1Hz, 1H) ; 6.40 (dd, J_{cis}=10.5Hz and J_{trans}=16.8Hz, 1H).

^{13}C NMR (CDCl$_3$,88 MHz) :14.1, 24.8, 24.8, 40.5, 58.9, 60.9, 110.7, 116.5, 136.2, 153.7, 168.0 .

MS (m/z) : 254 (M$^{+\cdot}$,29), 230(36), 209(30), 180(51), 160(49), 135(44), 93(49), 79(100), 67(24), 55(24).
Anal.Calcd for $C_{14}H_{22}O_4$: C, 66.11 ; H, 8.72 . Found : C, 59.85 ; H, 8.55 .

Diethyl 2-(2-methyl-3-vinyl-3-decene-2-yl) propanedioate 7l .

Procedure A (10 mmol scale ; 65° ; 24 h). Flash chromatography (90:10 P.E/AcOEt) of the filtered procuct gave 1.02 g (30 % yield) of a 80:20 mixture of the malonates (Z) and (E)- 7l [Z:E = 80:20 ratio based on ^{13}C NMR integration of vinylic carbons at 127.0 (Z-isomer) and 125.0 ppm (E-isomer)].

IR (neat) : 3070, 3040, 1755, 1730, 1620, 1235, 920 cm^{-1}.

^{1}H NMR (CDCl$_3$, 350 MHz) of the E + Z mixture : 0.88 (t, J=6.5Hz, 3H) ; 1.22 (t, J=7.2Hz, 6H) ; 1.2-1.4 (m, 8H) ; 1.3 (s, 6H) ; 2.09 (m, 2H) ; 3.60 (s, 1H) ; 4.12 (q, J=7.2Hz, 4H) ; 5.04 (d, J_{trans}=17.5Hz and J_{gem}=2.8Hz, 1H) ; 5.32(dd, J_{cis}=11.2Hz and J_{gem}=2.8Hz, 1H) ; 6.0 (t, J=7Hz, 1H) ; 6.17 (dd, J_{cis}=11.2Hz and J_{trans}=17.5Hz, 1H).

^{13}C NMR of (Z)-7l : 14.0, 14.0, 22.6, 24.9, 28.9, 29.2, 30.1, 31.7, 41.0, 59.0, 60.7, 119.7, 127.0 [125.0 for the related vinyl carbon of the minor isomer (E)-7l], 133.7, 143.8, 168.1 .

MS (m/z) (E + Z mixture) : 338 (M$^{+\cdot}$, 11), 178 (52), 160 (56), 107 (100), 55 (24).

Methyl 4-isopropenyl-2-phenylsulfonyl-4-dodecenoate 8a .

Procedure B (5 mmol scale ; 65°C ; 48h). Flash chromatography (80:20 P.E/AcOEt) of the filtered product gave 1.18 g (57 % yield) of a 80:20 mixture of the esters (E) and (Z)-8a [E:Z = 80:20 ratio based on ^{1}H NMR integration of vinylic protons at 5.64 (E-isomer) and 5.21 ppm (Z-isomer)].

IR (neat, E + Z mixture) : 3080, 3060, 1740, 1630, 1605, 1585, 1330, 1240, 1150, 760, 720, 630 cm^{-1}.

MS (m/z)(E+Z mixture) : 392 (M$^{+\cdot}$, 8), 251 (17), 165 (31), 125 (20), 121 (22), 107 (30), 93 (47), 91 (34), 77 (100), 71 (13), 59 (23), 57 (29).

^{1}H NMR (CDCl$_3$, 350 MHz) of (E)-8a : 0.88 (t,J=7Hz, 3H) ; 1.26 (br.s, 10H) ; 1.82 (s, 3H) ; 2.0 (m, 2H) ; 3.00 (AB part of an ABX syst., J_{AB}=14Hz, J_{AX}=2.8Hz and J_{BX}=11.8Hz, 2H) ; 3.59 (s, 3H) ; 4.14 (X part of an ABX syst. J_{AX}=2.8Hz and J_{BX}=11.2Hz, 1H) ; 4.80 (s, 1H) ; 4.88 (s, 1H) ; 5.64 (t, J=7Hz, 1H) ; 7.58 (m, 2H) ; 7.70 (m, 1H) ; 7.90 (m, 2H). [(Z)-8a isomer : vinylic proton at 5.21 ppm (t, J=7.1Hz, 1H)]

^{13}C NMR of (E)-8a : 14.0, 22.5, 21.3, 24.9, 28.3, 29.1, 29.2, 29.5, 31.7, 52.6, 69.4, 111.7, 129.3, 129.8, 132.7, 133.2, 134.2, 137.3, 142.2, 166.0.

^{13}C NMR of (Z)-8a : 14.0, 22.5, 21.9, 28.6, 29.1, 29.2, 29.5, 31.7, 33.5, 52.5, 69.7, 111.6, 129.3, 129.8, 130.6, 133.2, 134.2, 136.2, 141.8, 165.9 .

Methyl 2-phenylsulfonyl-4-vinyl-4-dodeceneoate 8b .

Procedure B (5.3 mmol scale ; 65°C ; 38h). Flash chromatography (90:10 P.E/AcOEt) of the crude product gave 1.42 g (71% yield) of a 30:70 mixture of the malonates (E) and (Z)-8b [E:Z = 30:70 ratio based on ^{1}H NMR integration of vinylic protons at 5.43 (E-isomer) and 5.29 ppm (Z-isomer)].
IR (neat, E+Z mixture): 3070, 3050, 3010, 1740, 1635, 1590, 1580, 1325, 1200, 1150, 760, 690 cm^{-1}.

Sulfonylester (Z)-8b .
^{1}H NMR (CDCl$_3$, 350 MHz) : 0.77 (t, J=7Hz, 3H) ; 1.14 (br.s, 10H) ; 1.96 (m, 2H) ; 2.77 (AB part of an ABX syst., J$_{AB}$=12.9Hz, J$_{AX}$=11.4Hz and J$_{BX}$=2.3Hz, 2H) ; 3.49 (s, 3H) ; 4.09 (X part of an ABX syst., J$_{AX}$=11.4Hz and J$_{BX}$=2.3Hz, 1H) ; 4.95 (d, J$_{cis}$=11.4Hz, 1H) ; 5.0 (d, J$_{trans}$=17.5Hz, 1H) ; 5.29 (t, J=7.4Hz, 1H) ; 6.44 (dd, J$_{cis}$=11.4Hz and J$_{trans}$=17.5Hz, 1H) ; 7.37-7.54 (m, 2H) ; 7.54-7.66 (m, 1H) ; 7.66-7.88 (m, 2H). [(E)-8b isomer : vinylic proton at 5.43 ppm (t, J=7.4Hz, 1H)].
^{13}C NMR (CDCl$_3$,88MHz) : 13.6, 22.2, 26.9, 28.5, 28.6, 29.0, 30.4, 31.3, 52.1, 69.3, 113.5, 128.7, 128.8, 130.0, 130.8, 133.9, 134.7, 136.8, 165.6.

(E)-8b : ^{13}C NMR (CDCl$_3$, 88MHZ) : 13.6, 22.2, 23.3, 27.6, 28.5, 28.7, 28.8, 31.3, 52.2, 68.7, 110.9, 128.7, 128.8, 130.8, 131.2, 136.8, 137.2, 138.4, 165.6.

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