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The palladium-catalyzed "vinylogous acetylenic Claisen rearrangement": a new vitamin A synthesis and a short path to allenic unsaturated carbonyls

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Summary – A new synthesis of retinal (vitamin A aldehyde) and various polyunsaturated carbonyls is proposed. Readily available mixed carbonates **1a-m** are neatly transformed into **2a-m** under the catalysis of palladium(0). In difficult cases (**1a**, **1b**, **1m**), ligand or catalyst tuning is effective for the regioisomeric control (**2/3**).

palladium / vinylogous Claisen rearrangement / retinal / vitamin A / allenes

Introduction

The Claisen rearrangement is now considered as the most versatile [3-3] sigmatropic shift for the construction of carbon frameworks [1]. It usually requires heating an allylic (or a propargylic) enol ether, which in turn results from an acid or metal-catalyzed vinyl exchange on the corresponding alcohol. There is a large body of evidence for an intramolecular, cyclic and concerted mechanism [1, 2].

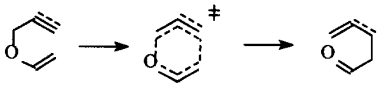


Fig 1

Over the years, the scope and synthetic utility of this transformation have been greatly increased by the introduction of the so-called Carroll [3], Claisen-Johnson [4], Claisen-Ireland [5] and Claisen-Eschenmoser [6] modifications. Notably, under certain circumstances, transition metals (mainly palladium(0) and (II) and aluminium(III) compounds) have been shown to be active catalysts [7]. For the palladium catalysts, according to the oxidation state, two modes of action have been postulated : a "cyclization-induced rearrangement" pathway [8] for Pd (II), and a "π-allyl-palladium rearrangement" pathway for Pd (0) [9]. An aza-Claisen rearrangement, which belongs to the second mechanistic family, has been found to proceed in the presence of both Pd (0) and protic acid catalysts [10]. For the aluminum-based catalysts, a charge-accelerated process is more likely, although not demonstrated [11].

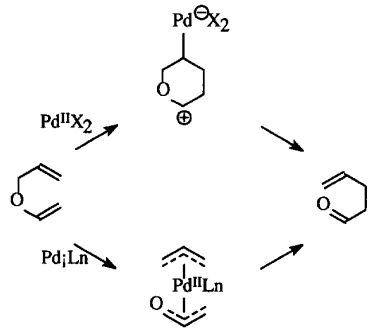


Fig 2

We were primarily interested in the Claisen rearrangement in connection with our studies towards new methods for the rapid building of isoprenoid backbones [12, 13]. For maximum synthetic efficiency, it was quickly recognized that a "vinylogous Claisen rearrangement" would be highly desirable since a five-carbon (rather than a three-carbon) atom homologation would be achieved in a single step (fig 4). Although such a transformation (formally an eight-membered sigmatropic rearrangement) is unprecedented, an elegant solution to this problem featured a tandem Claisen-Cope reaction, as reported by A Thomas in the early seventies [14]. This was used in a synthesis of citral [15]. However, this protocol is rather substrate limited and can sometimes be problematic to set up (fig 3).

Even more exciting, and not possible through this thermal tandem reaction, is the possibility of the catalysis of an "acetylenic vinylogous Claisen rearrangement", which may provide a powerful synthesis of polyconjugated aldehydes (and ketones), and a new route to such

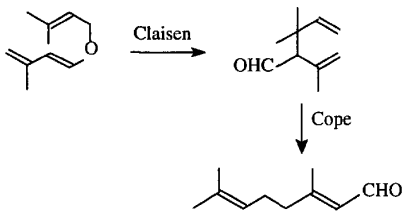


Fig 3

a highly valuable target as retinal (vitamin A aldehyde) [16].

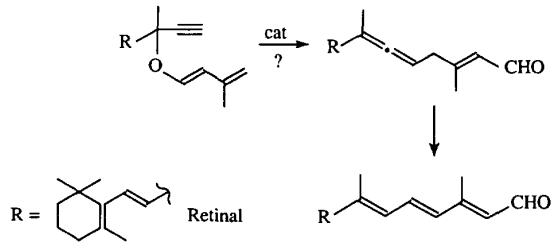


Fig 4

From an economic standpoint, I believe that this synthetic scheme is the ideal route to vitamin A, starting from readily available and inexpensive starting materials (ethynyl-β-ionol and prenal); it is short and avoids the troublesome recycling of stoichiometric synthetic auxiliaries. Mechanistically, I thought that a low-valent transition metal, which could oxidatively add to a propargylic dienol ether according to figure 5, would equilibrate to a bis-π-allyl metal species and give the desired linear aldehyde upon reductive elimination. Regeneration of the low-valent metal complex would then represent a true catalysis.

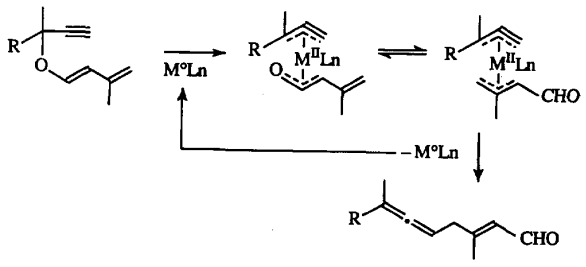
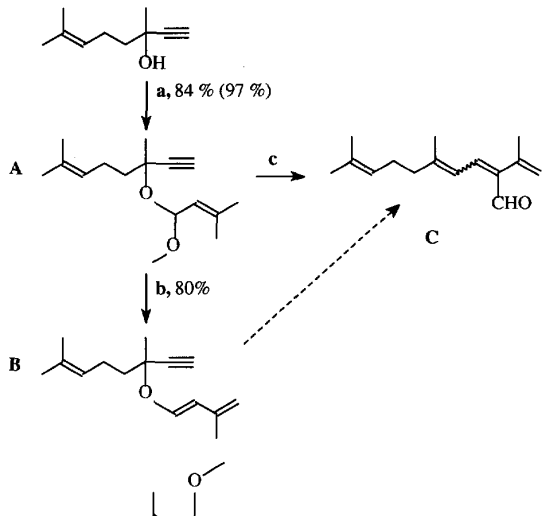


Fig 5

A new retinoid synthesis

Because of its simplicity and availability, I started by evaluating the behavior of the model dehydrolinalyloxy isoprene **B** with a variety of organometallic reagents. This substrate was prepared in a conventional way (see fig 6). Dehydrolinalol was heated with prenal dimethylacetal in the presence of toluic acid, which furnished the mixed acetal **A**, as a 55:45 mixture of diastereomers. Further heating under vacuum with azeotropic removal of methanol did not give the desired dienol ether **B** but an aldehyde **C** resulting from its thermal Claisen rearrangement. This could not be avoided. However, the milder Miller and McKean dealkoxylation procedure [17] was successful for this purpose.



Conditions : a) (2.5 equiv); 4-methylbenzoic acid (0.01 equiv); toluene; 50°C. b) TMSI (2 equiv) : $(TMS)_2NH$ (2.2 equiv); CCl_4; 0°C. c) 4-methylbenzoic acid (0.05 equiv); toluene; 50-80°C.

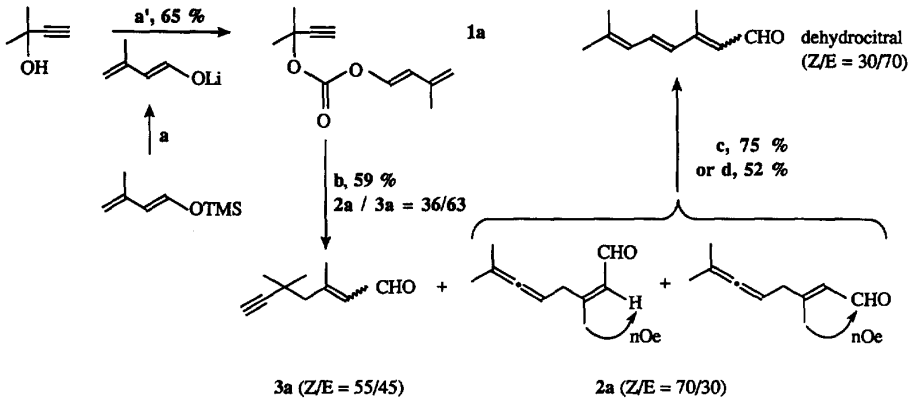
Fig 6

A broad catalyst screening of dehydrolinalyloxy-isoprene **B** was attempted and no other product was isolated apart from the branched polyconjugated aldehyde **C** (if any).

The crucial reductive metal-assisted C-O bond cleavage of **B** was difficult (even in the presence of added Lewis acid), and definitely not competitive with the easy thermal [3-3] sigmatropic rearrangement [18]. To facilitate this metal C-O insertion, we decided to move to a dienol carbonate which is a somewhat better leaving group than a dienol ether [19, 20]. The mixed carbonate **1a** was simply and efficiently prepared from methylbutynol, phosgene and the lithiated prenal enolate (generated from its trimethylsilyl enol ether according to Stork [21]). To my delight, this compound smoothly rearranged (with CO_2 extrusion) when treated with a catalytic amount (5%) of palladium tetrakis triphenylphosphine in THF (see fig 7) [28].

Two regioisomeric aldehydes were isolated by silica-gel chromatography, the minor product displayed typical NMR and IR patterns of allenes (**2a**; IR : 1 970 cm^{-1}; ^{13}C NMR : 202.8 and 203.2 ppm). The *Z* isomer for **2a** trisubstituted double bond was slightly favored (assignments made from NOE measurements between the methyl, and the vinylic and aldehydic hydrogens). Reconjugation of **2a** was quite easy under either basic (Na_2CO_3) or acidic (HBr) conditions and gave the known dehydrocitral.

Although I succeeded in preparing the new 3,7-dimethylocta-2,5,6-trienal **2a**, the regioselectivity of this transformation was not satisfactory. Reductive



Conditions : a) MeLi (1 equiv) ; THF-Et_2O ; −40°C. a') BuLi (1 equiv) ; THF-hexane ; −20°C then $COCl_2$ (1 equiv) ; toluene ; −20°C. b) $Pd(PPh_3)_4$ (0.05 equiv) ; THF ; 50-55°C. c) 48% HBr (0.05 equiv) ; acetone ; 0°C. d) Na_2CO_3 ; MeOH ; 25°C.

Fig 7

elimination at both ends of an equilibrated allenyl-propargyl palladium species occurred (see below and fig 12). At first sight, this observation was puzzling since the equilibrium between 3,3-dimethylallenyl palladium-X and 1,1-dimethylpropargyl palladium-X lies heavily on the left [22], allowing the characterization of 3,3-dimethylallenyl palladium chloride by X-ray crystallography [23].

To solve this problem, a short ligand optimization was carried out (see table I). The first observation was that a ligand was found necessary because palladium bis dibenzylideneacetone alone gave a complex mixture of products. Bidentate phosphines, alkyl phosphines (PBu_3, PCy_3), phosphites, amines and arsines were all found to be less effective than aromatic monodentate phosphines. Platinum tetrakis triphenylphosphine was not a good catalyst, whereas its nickel counterpart was. Notably, we observed a regioselective transformation **1a** → **2a** with this catalyst (entry 6 ; table I), although the yield was not as high as for the palladium catalysts.

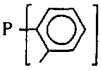
The most important fact is that the regioselectivity **2a/3a** could be returned to an acceptable level. For our preparative purposes, a combination of $Pd(dba)_2$ and tris naphthylphosphine was judged satisfactory.

I next turned my attention to the synthesis of retinal (C_{15} + C_5, fig 8). Ethynyl-β-ionol proved unsuitable as a starting material since its mixed carbonate was far to labile to be handled due to elimination.

To gain stability, ethynylretro-α-ionone [24] was readily prepared from β-ionone [25] and sequential reaction with phosgene and the prenal lithium enolate yielded the stable mixed carbonate **1b**. Rearrangement of **1b** with the previously optimized catalytic system gave aldehydes **2b** and **3b** (ratio 86:14), along with the β-elimination product, trienyne **4b**. This mixture could be purified by silica-gel chromatography, and **2b** was completely reconjugated with a catalytic amount of hydrobromic acid in aqueous acetone [26].

The retinal thus formed is a mixture of four stereomers (roughly E/Z = 70:30 for each trisubstituted double bond). However, by simple crystallization with

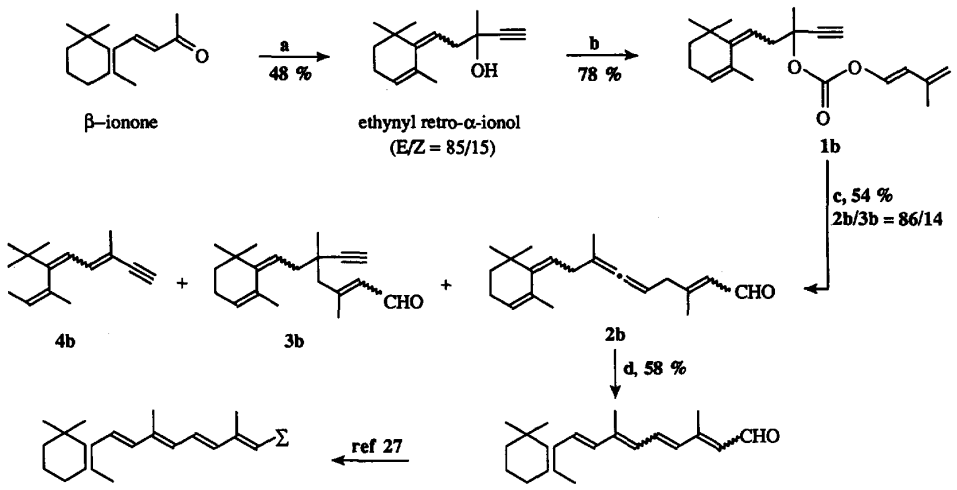
Table I. (**1a** → **2a** + **3a**).

Entry	Catalyst	Yield (%)	Selectivity (2a/3a)
1	$Pd(PPh_3)_4$	59	36/64
2	$Pd(dba)_2$ + 3 P[]$_3$	65	37/63
3	$Pd(dba)_2$ + 3 P[]$_3$	50	45/55
4	$Pd(dba)_2$ + 3 P[]$_3$	70	50/50
5	$Pd(dba)_2$ + 3 P[]$_3$	58	82/18
6	$Ni(PPh_3)_4$	33	100/0

All reactions were carried out with 5 mol % of catalyst, except for $Ni(PPh_3)_4$ (20 mol %).

hydroquinone, under equilibrating conditions, one can obtain pure all-*trans* retinal hydroquinone (RHQ) crystals in almost quantitative yield [27].

Upon completion of this straightforward and simple polyconjugated aldehyde synthesis, I decided to extend the scope of this new allene preparation to compounds other than terpenoid substrates. Several encouraging factors were considered : (i) palladium catalysis is easy to carry out experimentally, and is mild enough to allow the isolation of such sensitive compounds as **2a** or **2b** ; (ii) according to the substrate, regioselectivity can be tuned by the judicious choice of the ligands (and/or metals) ; (iii) besides vitamin A, many natural products



Σ = CHO : all-*E* retinal
Σ = CH_2OH : vitamin A
Conditions : a) see ref 24. b) see figure 7. c) $Pd(dba)_2$ (0.05 equiv); $P(Napht)_3$ (0.15 equiv); THF; 50°C. d) 48% HBr (0.10 equiv); acetone; 0°C.

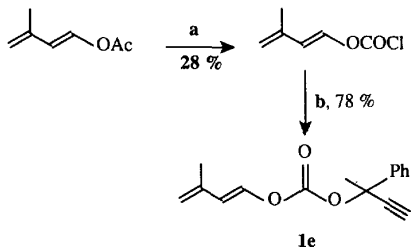
Fig 8

possess polyunsaturated backbones; (iv) two valuable functionalities are generated in this transformation, an allene and an α,β-unsaturated carbonyl, both of which can be used in further chemistry; and (v) the starting materials are readily available (propargylic alcohols and trimethylsilyl enol ethers).

A general rearrangement

For consistency in this study, I chose palladium tetrakis triphenylphosphine as a common catalyst and in most cases it proved to be sufficient. Mixed carbonates **1c,d,f-p** were prepared according to the general procedure described in the *Experimental section*, except for **1e** which needed a slightly different route, as depicted in figure 9. The results are divided into two parts : variation of the propargylic alcohol substituents (table II) and the dienolate moiety (table III, fig 10, 11).

Carbonates **1c-i** reacted readily when $Pd(PPh_3)_4$ was used as the catalyst, and the reactions ran to completion within 1-2 h at 50-60°C (table II). In most cases the allene **2** was the predominant product, but the



Conditions : a) Bu_3SnOMe [29] (0.95 equiv) then $COCl_2$ (0.95 equiv); toluene-CH_2Cl_2; 0°C → 25°C. b) 3-phenyl-3-butynol (0.75 equiv); BuLi (0.75 equiv); THF-hexane; −40°C.

Fig 9

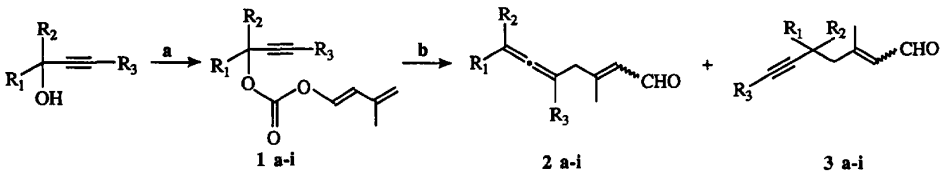
regioselectivity **2/3** ranged from 0:100 (for **1c**) to 100:0 (for **1f-h**).

Steric factors appear to play an important role [22]. When the R_1 and R_2 groups are small (hydrogens) the acetylene **3c** is exclusively formed, whereas for bulky substituents (**1f**; R_1, R_2 = 2,2,6-trimethylcyclohexane, entry 5) the opposite regioselectivity is observed. For intermediate situations (**1a**, **1d**, **1e**), mixtures are obtained, although direct correlation between the steric bulkiness of R_1 and R_2 and the **2/3** ratio is not obvious. On the other hand, R_3 substitution (alkyl **1g** or phenyl **1h**) seems to favor the formation of allene, a fact which could not be explained on purely steric grounds. Entry 8 shows that synthetically useful (and reactive) allenyl silane functionalities can be prepared by this method [30]. It should be mentioned that in all cases analytically pure allenes **2** and/or acetylenes **3** were purified by simple silica-gel flash chromatography.

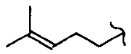
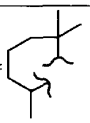
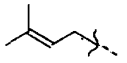
I next turned my attention to the preparation of other aldehydes and ketones by changing the dienolate structure. As can be seen from table III, allenes **2j-l** were obtained as the major compounds, but some by-products also arose. Again, it can be argued that competitive reductive elimination at unwanted positions competes.

Interestingly, very little reaction took place when a simple enol carbonate **1n** or a 2-substituted dienol carbonate **1p** was allowed to react with the catalyst $Pd(PPh_3)_4$ (fig 10). Going one step further, I tried to functionalize the terminal position of a trienolate (from sorbaldehyde) by rearrangement of carbonate **1m** (fig 11). Surprisingly instead of the desired allene **2m**, exclusive substitution at the propargylic site was observed with $Pd(PPh_3)_4$. No good explanation could be found for such an abnormal behavior. However, regioselectivity was almost completely reversed by simply switching to the nickel catalyst.

Table II

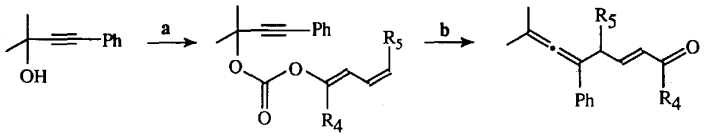


1 a-i 2 a-i 3 a-i

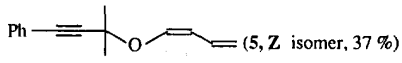
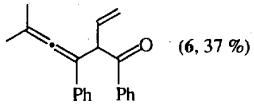
Entry	Substrate	Yield (step a) %	Yield * (step b) %	Selectivity (2/3)
1	**1a** ; $R_1 = R_2 = CH_3$, $R_3 = H$	65	59	36/64
2	**1c** ; $R_1 = R_2 = R_3 = H$	51	64	0/100
3	**1d** ; R_1 =  ; $R_2 = CH_3$; $R_3 = H$	71	51	90/10
4	**1e** ; R_1 = Ph ; $R_2 = CH_3$; $R_3 = H$	78	35	66/33
5	**1f** ; R_1, R_2 =  ; $R_3 = H$	31	69	100/0
6	**1g** ; $R_1 = R_2 = CH_3$; R_3 = 	73	51	100/0
7	**1h** ; $R_1 = R_2 = CH_3$; R_3 = Ph	90	90	100/0
8	**1i** ; $R_1 = {}^nC_7H_{15}$; $R_2 = H$; R_3 = TMS	75	42	* *

* Unoptimized yields.
** Some photodesilylation occurred (R_3 = TMS → H) during the reaction. The yield reported is for the pure **2i**, the selectivity being difficult to evaluate.
Conditions : a) as for figure 7. b) $Pd(PPh_3)_4$ (0.05 equiv); THF; 60°C.

Table III



1j-l 2j-l

Entry	Substrate	Yield (step a)	Yield (step b)	Other products (yield)
1	**1j** ; $R_4 = R_5 = H$	87 %	54 %	 (5, Z isomer, 37 %)
2	**1k** ; R_4 = Ph, $R_5 = H$	48 %	50 %	 (6, 37 %)
3	**1l** ; $R_4, R_5 = CH_2$–CH_2	60 %	82 %	

Conditions : a) BuLi (1 equiv), THF/hexane, −20°C then $COCl_2$ (1 equiv), toluene, −20°C then silyl enol ether (1.2 equiv), MeLi (1.1 equiv), TMEDA (1.1 equiv), −40°C. b) $Pd(PPh_3)_4$ (0.05 equiv), THF, 60°C.

Discussion

A likely mechanism for this new rearrangement is presented in figure 12. The active palladium catalyst (presumably $Pd(PAr_3)_2$) oxidatively inserts carbonates **1a-n**. After CO_2 loss, complex α, which is probably the first organometallic intermediate formed, can equilibrate to complexes β, γ or δ. The product distribution then reflects the relative concentrations and reductive elimination rates of these intermediates. The major factor governing these equilibria is the nature of the R_1 ... R_5 substituents, the influence of which can be puzzling

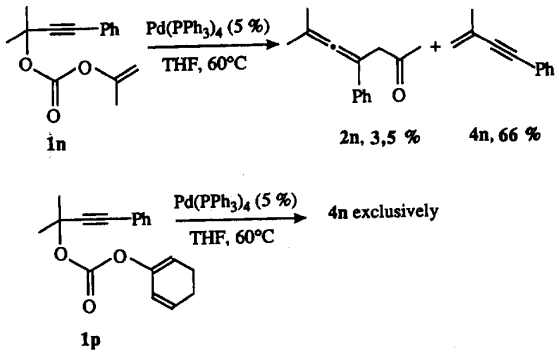
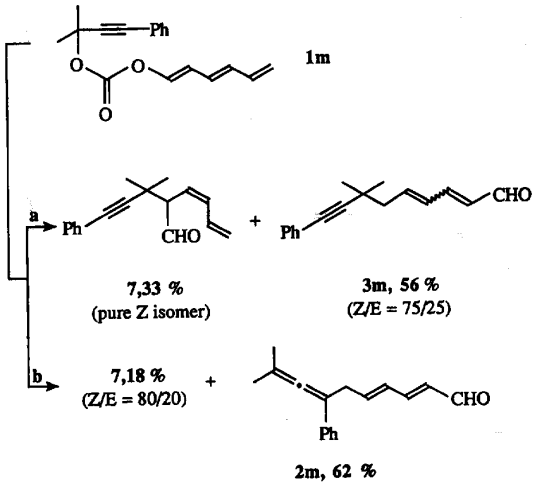


Fig 10



Conditions : a) as for table II. b) $Ni(COD)_2$ (0.20 equiv); PPh_3 (0.40 equiv); THF; 25°C; 3 h.

Fig 11

(see for instance the behavior of **1m** compared with **1j**). Nevertheless, some comments can be made, and several important trends have been identified.

First, to ensure carbon-carbon bond formation, complexes γ or δ must be energetically accessible. This is probably not the case with simple enol carbonates (such as **1n**) or 2-substituted dienol carbonates (such as **1p**), which cannot form stabilized π-allyl-Pd intermediates and remain as their oxygen-bonded Pd enolates (similar to complex β). A β-hydride elimination gives the corresponding enynes (**4h**, **4n**). This limitation is however of little relevance since the expected ketones (**2n** for instance) are well-established regular Claisen products [31].

Equilibrium between complex γ and δ is likely to be an important parameter in controlling the regioisomer ratio **2/3**. For instance, it was shown that bulky phosphines [32] do favor the formation of **2a** vs **3a** (table I) : **2a/3a** = 36:64 for PPh_3 ; **2a/3a** = 45:55 for P(*o*-tol)$_3$; and **2a/3a** = 82:18 for P(naphth)$_3$. Conversely, the basicity of the triarylphosphine is not crucial (compare entries 1 and 2, table I).

A similar observation can be made from table II, where, for a given phosphine (PPh_3), bulky substituents R_1 and R_2 have a strong "allene forming" effect (compare entries 2, 1 and 5, table II). Both experimental facts are explainable by a steric model involving repulsion between the ligand L and the (more or less) sterically demanding propargylallenyl appendage of complexes γ/δ [22].

The success of the transformation (**1** → **2/3**) probably lies in the rapid equilibria between the various organometallic species depicted in figure 12. In some cases, however, reductive elimination can occur competitively with these equilibria, and "non-thermodynamic" by-products are also formed.

For instance, the formation of dienol ether **5** can be explained by the reductive elimination of an intramolecularly coordinated Pd dienolate at the oxygen atom (corroborated by the exclusive *Z* stereochemistry of **5**, see fig 13). Similarly, the presence of **6** can be rationalized if the equilibrium between the two regioisomeric π-allyl Pd complexes shown in figure 13 (R_1 = Ph, R_2 = H) is slow enough to allow competitive bond formation next to the ketone.

Overall, we have shown that in all cases examined, exclusive (or preferential) formation of the "vinylogous Claisen" product **2** can be achieved from carbonates **1** by simple catalyst tuning (ligand and/or metal). The mildness of the catalysis was found to the a major asset in preparing sensitive (such as **2a**) or reactive (**2i**) allenes, and applied successfully in the synthesis of isoprenoid aldehydes, including the vitamin A aldehyde. Finally, although they were not studied here, optically active allenes should be obtained from the corresponding propargylic alcohols, through C-O → C-C chirality transfer.

Experimental section

General methods

All reactions were carried out under argon, with Fluka puriss grade solvents (used without further purification). TLC was carried out on precoated silica gel $60F_{254}$ plates (Merck) visualized by UV_{254} light and a $KMnO_4/K_2CO_3$ dip. Preparative flash chromatography was performed with 20-45 μm Amicon silica gel. A varian 3400 gas chromatograph with DB1 column (15 m × 0.53 mm) (Injector temperature = 150°C, detector temperature = 250°C, heating rate = 8°C/mm) was used whenever possible. NMR spectra were recorded on a Bruker AC 200 (^{1}H, 200 MHz) and AM 360 (^{1}H, 360 MHz; ^{13}C, 90 MHz) and chemical shifts are expressed relative to TMS as internal standard (solvent : $CDCl_3$). For IR spectra, a Perkin-Elmer 1750 FTIR was used, and for MS/HRMS a ZAB-3F Fisons instrument (EI^+).

3,7-Dimethyl-3-[(1-methoxy-3-methylbut-2-enyl)oxy]oct-6-en-1-yne **A**

A 100 mL flask equipped with a distillation apparatus and a vacuum regulator was charged with dehydrolinalol (6.85 g, 0.044 mol) and prenal dimethylacetal (12.61 g, 0.095 mol) in toluene (45 mL). Toluic acid (0.208 g, 1.5 mmol) was then added and the flask heated to reflux under a slight vacuum (120 mmHg, T = 56-60°C). Toluene azeotropic removal of methanol was carried out for 41 h, while a solution of prenal dimethylacetal (11 g, 0.084 mol) in toluene

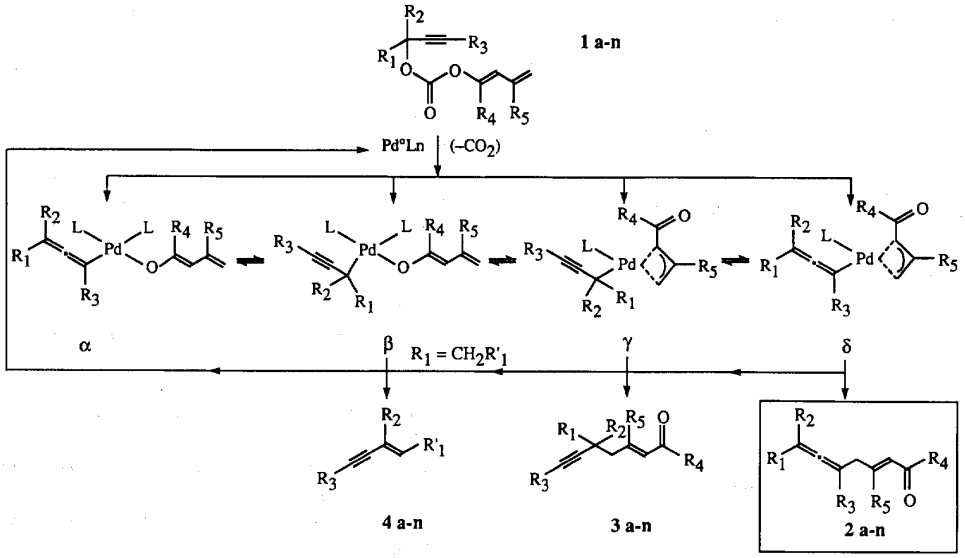


Fig 12

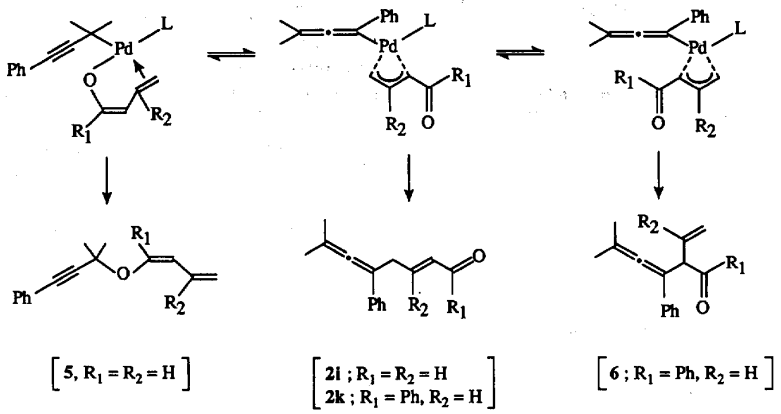


Fig 13

(115 mL) was continuously added. The evolution was monitored by gas chromatography. After cooling, the reaction mixture was washed with saturated Na_2CO_3, then with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The remaining oil (12.51 g), was analyzed by NMR and gas chromatography and proved to be a mixture of the mixed acetal A (75%), unreacted dehydrolinalol (7%), prenal dimethylacetal (12%), and toluene (6%). This crude product could not be purified by any chromatographic means without severe hydrolysis to the starting material. However, it was pure enough for the next step. Yield : 84% (96% based on recovered starting material).

^{1}H NMR (ppm), mixture (55:45) of two diastereomers : 1.33 and 1.47 (2 × s, 2 × CH_3); 2.45 (s, 1H); 3.20 and 3.27 (2 × s, 2 × OCH_3); 5.03 (m, 1H); 5.20 (m, 1H); 5.47 (d, J = 8 Hz, 0.55H); 5.54 (d, J = 8 Hz, 0.45H).

^{13}C NMR (ppm) : 23.0 and 23.2, 28.0 and 28.2, 42.8, 73.7 and 73.9, 85.2 and 85.5, 96.8, 131.7, 136.6.

3,7-Dimethyl-3-[(3-methylbuta-1,3-dien-1-yl)oxy]-oct-6-en-1-yne **B**

The crude mixed acetal **A** (2.99 g, purity 75%, 8.905 mmol) was dissolved in CCl_4 (25 mL) and hexamethyl disilazane (4.2 mL, 19.5 mmol). The solution was cooled to 0-5°C (ice bath) and TMSI added over 15 min. The reaction mixture was left for 1 h, then diluted with pentane (65 mL) and washed with 5% Na_2CO_3 (60 mL, then 2 × 40 mL), with water (2 × 40 mL) until neutral pH, dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (pentane/Et_3N 100:1) afforded **B** as a colorless oil (1.547 g, 7.08 mmol, 79%).

IR (cm^{-1}) : 3 295, 2 113, 1 650, 1 148, 906.

^{1}H NMR (ppm) : 1.44 (s, 3H); 1.56 (s, 3H); 1.77 (bs, 3H); 1.67-2.11 (m, 4H); 2.51 (s, 1H); 4.64 and 4.71 (m, 2H); 5.05 (m, 1H); 5.78 (d, J = 12.5 Hz, 1H); 6.69 (d, J = 12.5 Hz, 1H).

^{13}C NMR (ppm) : 17.6, 19.0, 22.9, 25,6, 27.1, 41.7, 74.6, 84.0, 112.0, 113.6, 123.3, 132,2 , 139.8, 142.9.

MS : m/z = 218, 135, 84.

HRMS for $C_{15}H_{22}O$: calc = 218.1671; found = 218.1666.

For the preparation of carbonates **1a-d**, **f-p**, the same protocol have been used and is exemplified for **1a**. For carbonates **1k** and **1l** (ketones) TMEDA (1 equiv) was added to the lithiated enolates prior to acylation.

Carbonic acid (1,1-dimethylprop-2-yn-1-yl) ester (3-methylbuta-1,3-dien-1-yl) ester **1a**

BuLi (1.6 M, hexanes, 15 mL, 24 mmol) was added to a cooled (−40°C) solution of methylbutynol (1.95 g, 23.2 mmol) in THF (20 mL). After 15 min, the cold alcoholate solution was poured on phosgene (1.93 M, toluene, 12.5 mL; 24.1 mmol) at −40°C over 5 min and left for an additional 15 min. Separately, MeLi (1.6 M, Et_2O, 16.5 mL, 26.4 mmol) was added dropwise to a solution of trimethylsiloxyisoprene (4.62 g, 29.6 mmol) in THF (20 mL) at −30°C. After 15 min, the chloroformate solution was added at −40°C and the resulting mixture allowed to stand for 30 min. Et_2O (60 mL) was then added followed by water (40 mL). The ethereal phase is washed with brine (2×20 mL), dried ($MgSO_4$) and concentrated. Chromatography (eluent : pentane/Et_2O 40:1 to 20:1) afforded carbonate **1a** (2.91 g, 14.98 mmol, 65%) as a colorless oil.

IR (cm^{-1}) : 3 296, 3 096, 1 765, 1 657, 873.

^1H NMR (ppm) : 1.75 (s, 6H) ; 1.85 (s, 3H) ; 2.61 (s, 1H) ; 4.94 (m, 2H) ; 6.14 (d, J = 12.5 Hz, 1H) ; 7.17 (d, J = 12.5 Hz, 1H).

^{13}C NMR (ppm) : 18.6, 28.6, 73.3, 75.0, 83.4, 116.6, 118.2, 138.1, 138.8.

MS : m/z = 84, 67, 41.

Anal (%) : calc for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found : C, 67.93; H, 7.28.

The palladium-catalyzed transformation of carbonates **1a** into **2a** and **3a** is given as an example. This procedure is common to all other carbonates (**1b-p**).

3,7-Dimethylocta-2,5,6-trienal **2a** *and 3,5,5-trimethylhept-2-en-6-ynal* **3a**

Carbonate **1a** (0.343 g, 1.77 mmol) is dissolved in THF (6 mL) at 25°C. Palladium tetrakis triphenylphosphine (0.100 g, 0.086 mmol) was added under argon, and the solution warmed to 55-60°C until disappearance of carbonate **1a** (TLC, Et_2O/pentane 1:10). The crude reaction mixture was cooled, concentrated *in vacuo* at cold, and chromatographed (Et_2O/pentane 1:10) at once, since allenic aldehyde **2a** was rather unstable and decomposed readily in the presence of the catalytic system. Aldehyde **2a** was eluted in the first fraction (0.0568 g, 0.38 mmol, 21%) and aldehyde **3a** in the second (0.1019 g, 0.68 mmol, 38%). Aldehyde **2a**, mixture of Z/E = 70/30 stereomers.

IR (cm^{-1}) : 1 970, 1 674.

^1H NMR (ppm) : Z isomer : 1.67 (d, J = 2.5 Hz, 4.2H) ; 2.00 (d, J < 1 Hz, 2.1H) ; 3.18 (d, J = 6.5 Hz, 1.4H) ; 5.03 (m, 0.7H) ; 5.90 (bd, $J \approx$ 8 Hz) ; 9.85 (d, J = 8 Hz, 0.7H). E isomer : 1.69 (d, J = 2.5 Hz, 1.8H) ; 2.19 (d, J < 1 Hz, 0.9H) ; 2.84 (d, J = 6.5 Hz, 0.6H) ; 4.91 (m, 0.3H) ; 5.96 (bd, $J \approx$ 8 Hz) ; 10.00 (d, J = 8 Hz, 0.3H).

^{13}C NMR (ppm) : Z isomer : 20.3, 24.4, 32.5, 85.6, 97.3, 128.2, 162.2, 190.8, 203.2. E isomer : 17.2, 20.3, 40.8, 84.4, 95.9, 127.4, 162.5, 191.2, 202.8.

MS : m/z = 150,135,121.

HRMS for $C_{10}H_{14}O$: calc = 150,1045; found = 150,1044.

Aldehyde **3a**, mixture of Z/E = 55/45 stereomers.

IR (cm^{-1}) : 3 305, 2 110, 1 675, 1 630.

^1H NMR (ppm) : Z isomer : 1.33 (s, 3.3H) ; 2.14 (d, J < 1 Hz, 1.65H) ; 2.20 (s, 1.1H) ; 6.05 (bd, $J \approx$ 8 Hz, 0.55H) ; 9.93 (d, J = 8 Hz, 0.55H). E isomer : 1.28 (s, 2.7H) ; 2.33 (s, 0.9H) ; 2.35 (d, J < 1 Hz, 1.35H) ; 5.93 (bd, $J \approx$ 8 Hz, 0.45H) ; 10.03 (d, J = 8 Hz, 0.45H).

MS : m/z = 150, 135, 121.

Carbonic acid [3-methyl-5-(2,6,6-trimethylcyclohex-2-en-1-ylidene)pent-1-yn-3-yl] ester (3-methylbuta-1,3-dien-1-yl) ester **1b**

This carbonate is an E/Z = 90:10 stereomer mixture (exocyclic double bond).

IR (cm^{-1}) : 3 294, 3 095, 2 122, 1 767, 1 658, 1 612, 1 245, 932, 885.

^1H NMR (ppm) : E isomer : 1.19 (s, 3H) ; 1.21 (s, 3H) ; 1.48 (t, J = 6 Hz, 2H) ; 1.77 (s, 3H) ; 1.85 (bs, 3H) ; 2.09 (m, 2H) ; 2.65 (s, 1H) ; 3.06 (m, 2H) ; 4.93 (m, 2H) ; 5.50 (bt, $J \approx$ 7 Hz, 1H) ; 5.68 (m, 1H) ; 6.15 (d, J = 12.5 Hz, 1H) ; 7.18 (d, J = 12.5 Hz, 1H).

^{13}C NMR (ppm) : 18.6, 21.8, 28.2, 28.3, 34.7, 40.1, 41.0, 74.6, 82.6, 116.6, 117.3, 118.2, 133.3, 137.7, 138.1, 145.9, 150.5.

MS : m/z = 328 (w), 284, 201.

HRMS for $C_{20}H_{28}O$: calc = 284,2140; found = 284,2143.

3,7-Dimethyl-9-(2,6,6-trimethylcyclohex-2-en-1-ylidene)nona-2,5,6-trienal **2b**

This aldehyde is a mixture of stereomers : E/Z = 90:10 for the exocyclic double bond (C_9) and E/Z = 40:60 for the α,β-unsaturated double bond (C_2).

IR (cm^{-1}) : 1 966, 1 677, 1 635.

^1H NMR (ppm) : 1.99 (s, 6H) ; 1.46 (t, $J \approx$ 6 Hz, 2H) ; 1.69-1.81 (m, 6H) ; 2.06 (m, 2H) ; 2,98 (m, 2H) ; 5.40 (b, $J \approx$ 7 Hz, 1H) ; 5.65 (m, 1H). C_2-Z isomer : 1,97 (d, J < 1 Hz, 1.8H) ; 3.20 (dd, J = 6.5 Hz, 2.5 Hz, 1,2H) ; 5.16 (m, 0.6H) ; 5.89 (bd, J = 8 Hz) ; 9.90 (d, J = 8 Hz, 0.6H). C_2-E isomer : 2.17 (d, J < 1 Hz, 1.2H) ; 2.86 (d, J = 7 Hz, 0.8H) ; 5.06 (m, 0.4H) ; 5.95 (bd, $J \approx$ 8 Hz) ; 9.99 (d, J = 8 Hz, 0.4H).

MS : m/z = 284, 269, 255.

HRMS for $C_{20}H_{28}O$: calc = 284,2140; found = 284,2143.

Reconjugation of **1b** *or* **2b**

• *Acidic conditions*

Freshly prepared **2b** (0.125 g, 0.439 mmol) was dissolved in acetone (2 mL) and cooled to 0-5°C (ice bath). A 0.126 M solution of HBr in acetone (0.35 mL, 0.044 mmol) was added under argon. The yellowish solution turns dark green and complete isomerization was observed after 1 h (TLC, Et_2O/pentane 1:10). Saturated HCO_3Na (2 mL) was added, and the reaction mixture extracted with pentane (2 × 20 mL). Flash chromatography (Et_2O/pentane 1:10 → 1:5) yielded retinal as a deeply coloured (orange) gum (0.0728 g, 0.256 mmol, 58%).

• *Basic conditions*

Freshly prepared **2a** (0.200 g, 1.33 mmol) was dissolved in methanol (2 mL). At room temperature Na_2CO_3 (0.100 g) was added and the evolution followed either by TLC (Et_2O/pentane 1:10) or GC. After disappearance of **2a**, the reaction mixture was filtered, concentrated *in vacuo*, and chromatographed (Et_2O/pentane 1:10) to give dehydrocitral (0.104 g, 0.69 mmol, 52%).

Carbonic acid (prop-2-yn-1-yl) ester (3-methylbuta-1,3-dien-1-yl) ester **1c**

IR (cm^{-1}) : 3 297, 2 133, 1 763, 1 660, 1 612, 934, 892, 686, 640.

^1H NMR (ppm) : 1.84 (bs, 3H) ; 2.56 (t, J = 2.5 Hz, 1H) ; 4,79 (d, J = 2,5 Hz, 2H) ; 4.94 (m, 2H) ; 6.16 (d, J = 12.5 Hz, 1H) ; 7.12 (d, J = 12.5 Hz, 1H).

^{13}C NMR (ppm) : 18.3, 55.6, 76.1, 76.4, 117.3, 119.1, 137.9, 138.1, 152.7.

MS : m/z = 166, 121, 83, 55.

HRMS for $C_9H_{10}O_3$: calc = 166,0630; found = 166,0631.

3-Methylhept-2-en-6-ynal **3c**

Mixture of Z/E = 45:55 stereomers.

IR (cm^{-1}) = 3 290, 2 118, 1 674, 1 635, 1 614, 650.

^{1}H NMR (ppm) : 2.04 (t, J = 2.5 Hz, 1H); 2.41-2.54 (m, 3H). Z isomer : 2.02 (d, J < 1 Hz, 1.35H); 2.80 (t, J = 7 Hz, 0.90H); 5.98 (bd, $J \sim 8$ Hz, 0.45H); 5.98 (bd, $J \approx 8$ Hz, 0.45H); 9.98 (d, J = 8 Hz, 0.45H). E isomer : 2.21 (d, J < 1 Hz, 1.65H); 5.92 (bd, $J \approx 8$ Hz, 0.55H); 10.02 (d, J = 8 Hz, 0.55H).

^{13}C NMR (ppm) : Z isomer : 17.5, 24.4, 30.7, 70.3, 81.9, 129.6, 160.3, 190.4. E isomer : 16.4, 17.2, 38.6, 69.5, 82.2, 127.7, 160.6, 190.8.

MS : m/z = 122(w), 121, 107, 93.

HRMS for C_8H_9O : calc = 121,0653; found : 121,0654.

Carbonic acid (3,7-dimethyloct-6-en-1-yn-3-yl) ester (3-methylbuta-1,3-dien-1-yl) ester **1d**

IR (cm^{-1}) : 3 296, 3 095, 2 120, 1 763, 1 657, 1 255, 886.

^{1}H NMR (ppm) : 1.63 (s, 3H); 1.69 (s, 3H); 1.75 (s, 3H); 1.84 (s, 3H); 1.80-2.30 (m, 4H); 2.64 (s, 1H); 4.94 (m, 2H); 5.12 (m, 1H); 6.15 (d, J = 12.5 Hz, 1H); 7.18 (d, J = 12.5 Hz, 1H).

^{13}C NMR (ppm) : 17.6, 18.6, 22.8, 25.6, 26.1, 41.1, 74.4, 78.0, 82.6, 116.6, 118.2, 122.7, 132.6, 137.7, 138.1, 150.5.

MS : m/z = 247,203, 135, 84, 69.

HRMS for $C_{15}H_{19}O_3$: calc = 247,1334; found = 247,1329.

3,7,11-Trimethyldodeca-2,5,6,10-tetraenal **2d**

Mixture of Z/E = 62:38 stereomers.

IR (cm^{-1}) : 2 755, 1 965, 1 680, 1 636.

^{1}H NMR (ppm) : 1.60 (s, 3H); 1.68 (bs, 6H); 1.86-2.13 (m, 4H); 4.95-5.18 (m, 2H). Z isomer : 1.99 (d, J = 2 Hz); 3.19 (d, J = 6.5 Hz, 1.25H); 5.89 (bd, $J \approx 8$ Hz, 0.60H); 9.91 (d, J = 8 Hz, 0.6H). E isomer : 2.19 (d, J = 2 Hz); 2.85 (d, J = 7 Hz, 0.75H); 5.96 (bd, $J \approx 8$ Hz, 0.4H); 10.00 (d, J = 8 Hz, 0.4H).

^{13}C NMR (ppm) : Z-isomer : 17.6, 18.8, 25.0, 25.6, 26.2, 32.6, 33.9, 87.0, 101.7, 123.8, 128.3, 131.7, 162.3, 190.8, 202.5. E isomer : 17.3, 17.6, 18.9, 25.6, 26.2, 33.9, 41.0, 85.9, 100.3, 123.8, 127.5, 131.7, 162.5, 191.2, 202.8.

MS : m/z = 218, 203, 200, 175.

HRMS for $C_{15}H_{22}O$: calc = 218,1671; found 218, 1664.

Carbonic acid (3-phenylbut-1-yn-3-yl) ester (3-methylbuta-1,3-dien-1-yl) ester **1e**

Tributyltin methoxide (7 mL, 24.3 mmol) was added at 0°C under argon to 3.26 g (25.8 mmol) of freshly distilled 1-acetoxyisoprene [29]. The mixture was warmed to room temperature and left for 30 min. After dilution with CH_2Cl_2 (20 mL) the [(tributylstannyl)oxy]isoprene was added to a toluenic solution of phosgene (1.93 M, 12.5 mL, 24.0 mmol) at 0°C. After 15 min, the crude reaction mixture is concentrated *in vacuo* (under N_2), then bulb-to-bulb distilled (T = 110°C, P = 50 mbar) to give 1.32 g of a clear liquid. (^{1}H NMR purity = 74%; yield = 28%). Isopren-1-yl chloroformiate was to unstable to be fully characterized, and so its structure was ascertained by ^{1}H NMR and its subsequent transformation into **1e**.

3-Phenylbut-1-yn-3-ol (0.664 g, 4.54 mmol) was dissolved in THF (5 mL). After cooling (−40°C), BuLi (1.6 M, hexanes, 3 mL, 4.8 mmol) was added dropwise, and the reaction left for 10 min. Isoprenyl chloroformate (6 mmol) in THF (1.5 mL) was added at −40°C. After standing for 30 min, the reaction mixture was diluted with Et_2O (50 mL) and successively washed with saturated $NaHCO_3$; 5% Et_3N/H_2O; saturated NaCl. The crude product was dried ($MgSO_4$), concentrated *in vacuo*, and chromatographed (Et_2O/pentane, 1:10) to give **1e** as a colorless oil (0.911 g, 3.55 mmol, 78%).

IR (cm^{-1}) : 3 290, 2 126, 1 768, 1 657, 1 495, 1 250, 1 083, 745, 700.

^{1}H NMR (ppm) : 1.78 (s, 3H); 1.98 (s, 3H); 2.90 (s, 1H); 4.92 (m, 2H); 6.13 (d, J = 12.5 Hz, 1H); 7.10 (d, J = 12.5 Hz, 1H); 7.30-7.70 (m, 5H).

MS : m/z = 212, 197, 129.

3-Methyl-7-phenylocta-2,5,6-trienal **2e**

Mixture of Z/E = 78:22 stereomers.

IR (cm^{-1}) : 2 755, 1 950, 1 673.

^{1}H NMR (ppm) : 2.10 (d, J = 2.5 Hz, 3H); 5.37-5.58 (m, 1H); 7.20-7.70 (m, 5H). Z isomer : 2.01 (d, J < 1 Hz, 2.4H); 3.33 (dd, J = 7 Hz, 2.5 Hz, 1.6H); 5.90 (bd, $J \approx 8$ Hz, 0.8H); 9.95 (d, J = 8 Hz, 0.8H). E isomer : 2.20 (d, J < 1 Hz, 0.6H); 2.99 (d, J = 7 Hz, 0.4H); 6.01 (bd, $J \approx 8$ Hz, 0.2H); 10.01 (d, J = 8 Hz, 0.2H).

MS : m/z = 212, 197, 169.

3,5-Dimethyl-5-phenylhept-2-en-6-ynal **3e**

Single Z isomer.

IR (cm^{-1}) : 3 244, 2 870, 2 775, 2 106, 1 663, 1 627, 1 600, 1 580, 1 493.

^{1}H NMR (ppm) : 1.68 (d, J < 1 Hz, 3H); 1.78 (s, 3H); 2.52 (s, 1H); 2.89 (d, J = 13 Hz, 1H); 3.18 (d, J = 13 Hz, 1H); 5.92 (bd, $J \approx 8$ Hz, 1 Hz); 7.2-7.6 (m, 5H); 9.72 (d, J = 8 Hz, 1H).

MS : m/z = 212, 197, 179, 129.

Carbonic acid (1-ethynyl-2,2,6-trimethylcyclohexyl) ester (3-methylbuta-1,3-dien-1-yl) ester **1f**

IR (cm^{-1}) : 3 305, 3 094, 2 114, 1 768, 1 656, 1 235, 1 460, 883.

^{1}H NMR (ppm) : 1.06 (d, J = 6.5 Hz, 3H); 1.10 (s, 3H); 1.20 (s, 3H); 1.20-1,80 (m, 7H); 1.84 (s, 3H); 2.80 (s, 1H); 4.92 (m, 2H); 6.13 (d, J = 12 Hz, 1H); 7.19 (d, J = 12 Hz, 1H).

^{13}C NMR (ppm) : 17.0, 18,6, 20.6, 20.9, 27.7, 31.7, 36.8, 37.9, 40.5, 78.0, 79.8, 90.1, 116.2, 117.7, 138.2, 138.3, 150.8.

MS : m/z = 276(w), 261, 149, 84.

HRMS for $C_{16}H_{21}O_3$: calc = 261,1491; found = 261,1499.

Anal (%) : Calc for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found : C, 74.17; H, 9.08.

3-Methyl-6-(2,6,6-trimethylcyclohexylidene)hexa-2,5-dienal **2f**

Mixture of Z/E = 60:40 stereomers.

IR (cm^{-1}) : 2 925, 1 956, 1 678, 1 456.

^{1}H NMR (ppm) : 0.87-1.10 (8s, 9H); 1.20-1.80 (m, 6H); 2.03 (d, J < 1 Hz, 1,8H); 2.19 (d, J < 1 Hz); 2.88 and 2.90 (2 × d, J = 7 Hz, 0.84H); 3.20 and 3.22 (2 × d, $J \approx 7$ Hz, 1.2H); 5.08-5.35 (m, 1H); 5.88 and 5.96 (2×bd, $J \approx 8$ Hz, 1H); 9.92; 9.95; 10.00 (3 × d, J = 8 Hz, 1H).

MS : m/z = 232, 217, 199.

Carbonic acid (2,6-dimethylhept-1-en-4-yn-6-yl) ester (3-methylbuta-1,3-dien-1-yl) ester **1g**

IR (cm^{-1}) : 3 090, 2 990, 2 248, 1 763, 1 680, 1 657, 1 612, 1 255, 1 123, 933, 893.

^1H NMR (ppm) : 1.73 (s, 6H); 1.78 (s, 3H); 1.85 (s, 3H); 2.94 (bs, 2H); 4.84 (m, 1H); 4.92 (m, 1H); 4.95 (m, 1H); 5,02 (m, 1H); 6.11 (d, J = 12 Hz, 1H); 7.17 (d, J = 12 Hz, 1H).

^{13}C NMR (ppm) : 18.6, 22.0, 27.3, 28.9, 75.8, 82.5, 82.9, 111.7, 116.3, 117.9, 137.8, 138.2, 139.9, 150.5.

MS : m/z = 248 (w), 121,84.

HRMS for $C_{15}H_{20}O_3$: calc = 248,1412; found : 248,1408.

Anal (%) calc for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found : C, 72.70; H, 8.25.

3,7-Dimethyl-5-(1-methylprop-2-en-1-yl)octa-2,5,6-trienal **2g**

Mixture of Z/E = 80:20 stereomers.

IR (cm^{-1}) : 2 977, 2 935, 1 970, 1 680, 1 680, 1 638, 893.

^1H NMR (ppm) : 1.64 (s, 6H); 1.72 (bs, 3H); 4.75-4.80 (m, 2H); 5.90 (bd, $J \approx$ 8 Hz, 1H). Z isomer : 1.96 (d, J < 1 Hz, 2.4H); 2.69 (s, 1.6H); 9.81 (d, J = 8 Hz, 0.8H). E isomer : 2.16 (d, J < 1 Hz, 0.6H); 2.61 (s, 0.4H); 2.77 (s, 0.4H); 10.00 (d, J = 8 Hz , 0.2H).

MS : m/z = 204, 189, 186, 171.

Carbonic acid (3-methyl-1-phenylbut-1-yn-3-yl) ester (3-methylbuta-1,3-dien-1-yl) ester **1h**

IR (cm^{-1}) : 2 231, 1 763, 1 678, 1 657, 1 255, 1 120, 933, 880, 757, 692.

^1H NMR (ppm) : 1.83 (s, 6H); 1.85 (s, 3H); 4.93 (m, 2H); 6.15 (d, J = 12.5 Hz, 1H); 7.20 (d, J = 12.5 Hz, 1H); 7.26-7.48 (m, 5H).

^{13}C NMR (ppm) : 18.7, 28.8, 75.9, 85.0, 88.7, 116.5, 118.0, 122.1, 128.2, 128.5, 131.8, 137.8, 138.1, 150.5.

MS : m/z = 270 (w), 143, 84.

HRMS for $C_{17}H_{18}O_3$: calc : 270,1256; found : 270,1254.

Anal (%) : calc for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found : C, 74.98; H, 6.90.

3,7-Dimethyl-5-phenylocta-2,5,6-trienal **2h**

Mixture of Z/E = 87:13 stereomers.

IR (cm^{-1}) : 1 954, 1 676, 760, 695.

^1H NMR (ppm) : 5.97 (bd, $J \approx$ 8 Hz, 1H); 7.17-7.40 (m, 5H). Z isomer : 1.76 (s, 5.1H); 2.00 (d, J < 1 Hz, 2.55H); 3.63 (s, 1.7H); 9.91 (d, J = 8 Hz, 0.85H). E isomer : 1.81 (s, 0.9H); 2.22 (d, J < 1 Hz, 0.45H); 3.32 (s, 0.3H); 10.00 (d, J = 8 Hz, 0.15H).

^{13}C NMR (ppm) : 19.9, 25.5, 33.6, 100.6, 101.1, 125.8, 126.7, 128.4, 129.0, 137.4, 161.6, 191.0, 202.5.

MS : m/z = 226, 211, 143.

HRMS for $C_{16}H_{18}O$: calc : 226,1358; found : 226,1353.

1-(Trimethylsilyl)dec-1-yn-3-ol

IR (cm^{-1}) : 3 330, 2 927, 2 858, 2 172, 1 250, 1 050, 1 020, 845, 760.

^1H NMR (ppm) = 0.10 (s, 9H); 0.82 (bt, $J \approx$ 7 Hz, 3H); 1.23-1.61 (m, 12H); 1.75 (s, 1H); 4.28 (m, 1H).

^{13}C NMR (ppm) : −0.13, 14.0, 22.6, 25.1, 29.1, 31.7, 37.7, 62.9, 89.3, 106.9.

MS : m/z = 211.

Carbonic acid [1-(trimethylsilyl)dec-1-yn-3-yl] ester (3-methylbuta-1,3-dien-1-yl) ester **1i**

IR (cm^{-1}) : 2 180, 1 762, 1 658, 1 612, 1 260, 1 250, 884, 845, 760.

^1H NMR (ppm) : 0.18 (s, 9H); 0.88 (m, 3H); 1.20-1.50 (m, 10H); 1.87 (s, 3H); 4.95 (m, 2H); 5.27 (t, J = 6.5 Hz, 1H); 6.16 (d, J = 12.5 Hz, 1H); 7.17 (d, J = 12.5 Hz, 1H).

MS : m/z = 209,84.

3-Methyl-5-(trimethylsilyl)tetradeca-2,5,6-trienal **2i**

Mixture of Z/E = 65:35 stereomers.

IR (cm^{-1}) : 2 956, 2 927, 2 855, 1 936, 1 681, 1 250, 842, 756.

^1H NMR (ppm) : 0.92 (bt, $J \approx$ 7 Hz, 3H); 1.20-1.85 (m, 12H); 4.82 (m, 1H); 5.83 (m, 1H). Z isomer : 0.06 (s, 5.85H); 1.88 (bs, 1.95H); 3.09 (m, 1,3H); 9.73 (d, J = 8 Hz, 0.65H). E isomer : 0.02 (s, 3.15H); 2.09 (bs, 1H); 2.79 (m, 0.7H); 9.92 (d, J = 8 Hz, 0.35H).

MS : m/z = 292, 277, 207.

Anal (%) : calc for $C_{18}H_{32}OSi$: C, 73.90; H, 11.02. Found : C, 73.79; H, 11.11.

Carbonic acid (3-methyl-1-phenylbut-1-yn-3-yl) ester (buta-1,3-dien-1-yl) ester **1j**

IR (cm^{-1}) : 2 230, 1 766, 1 662, 1 260, 1 120, 996, 923, 875.

^1H NMR (ppm) : 1.83 (s, 6H); 5.04 (dd, J = 10.5 Hz, 1 Hz, 1H); 5.21 (dd, J = 16 Hz, 1 Hz, 1H); 6.05 (dd, J = 11 Hz, 10.5 Hz, 1H); 6.27 (ddd, J = 16 Hz, 11 Hz, 10.5 Hz, 1H); 7.25-7.50 (m, 5H).

^{13}C NMR (ppm) : 29.8, 76.0, 85.1, 88.6, 115.8, 117.2, 122.1, 128.1, 128.6, 131.3, 131.8, 140.0, 150.1.

MS : m/z = 143, 70.

7-Methyl-5-phenylocta-2,5,6-trienal **2j**

Single E isomer.

IR (cm^{-1}) : 2 737, 1 954, 1 692, 1 640, 1 598, 1 493, 974.

^1H NMR (ppm) : 1.81 (s, 6H); 3.43 (dd, J = 6.5 Hz, 1.5 Hz, 1H); 6.22 (ddt, J = 16 Hz, 8 Hz, 1.5 Hz, 1H); 6.95 (dt, J = 16 Hz, 6.5 Hz, 1H); 7.17-7.37 (m, 5H); 9.53 (d, J = 8 Hz, 1H).

^{13}C NMR (ppm) : 20.2, 34.0, 99.7, 99.8, 125.8, 126.6, 128.4, 133.7, 136.8, 155.9, 193.7, 200.3.

MS : m/z = 212, 197, 183, 143.

3-[(Buta-1,3-dien-1-yl)oxy]-3-methyl-1-phenylbut-1-yne **5**

Single Z isomer.

IR (cm^{-1}) : 3 083, 3 055, 2 987, 2 227, 1 646, 1 247, 1 140, 1 000, 890, 757, 692.

^1H NMR (ppm) : 1.63 (s, 6H); 4.92 (bd, $J \approx$ 10 Hz, 1H); 5.10 (bd, $J \approx$ 17 Hz, 1H); 5.24 (dd, J = 11 Hz, 6 Hz, 1H); 6.52 (bd, $J \approx$ 6 Hz); 6.74 (ddd, J = 17 Hz, 11 Hz, 10 Hz, 1H); 7.25-7.45 (m, 5H).

^{13}C NMR (ppm); 29.3, 73.2, 85.3, 90.1, 108.9, 113.0, 122.3, 128.2, 128.4, 131.7, 131.8, 141.5.

MS : m/z = 212 (w), 143.

Carbonic acid (3-methyl-1-phenylbut-1-yn-3-yl) ester (1-phenylbuta-1,3-dien-1-yl) ester **1k**

Single Z isomer.

IR (cm^{-1}) : 2 229, 1 769, 1 644, 1 385, 1 366, 1 232, 1 123, 978, 914, 888.

^1H NMR (ppm) : 1.83 (s, 6H); 5.20 (dd, J = 10 Hz, 1.5 Hz, 1H); 5.41 (dd, J = 16.5 Hz, 1.5 Hz, 1H); 6.42 (d, J = 11 Hz, 1H); 6.67 (ddd, J = 16.5 Hz, 11 Hz, 10 Hz, 1H); 7.22-7.56 (m, 10H).

^{13}C NMR (ppm) : 28.7, 76.2, 84.9, 88.9, 117.4, 119.5, 122.2, 124.5, 128.1, 128.5, 128.6, 129.8, 131.8, 134.3, 146.5, 150.5.

MS : m/z = 288, 160, 143.

HRMS for $C_{21}H_{20}O$: calc : 288, 1514; found : 288, 1506.

1,5-Diphenyl-7-methylocta-2,5,6-trien-1-one **2k**

Single E isomer.

IR (cm^{-1}) : 1 954, 1 671, 1 385, 1 361, 985, 972, 760, 695.

^1H NMR (ppm) : 1.83 (s, 6H); 3.42 (dd, J = 6 Hz, 1 Hz, 2H); 6.92 (dt, J = 17.5 Hz, 1 Hz, 1H); 7.05-7.60 (m, 9H); 7.84-7.91 (m, 2H).

^{13}C NMR (ppm) : 20.3, 34.1, 99.5, 100.5, 125.9, 126.5, 127.3, 128.6, 132.5, 137.2, 137.9, 147.2, 191.3, 202.6.

MS : m/z = 288, 273, 183, 143, 105.

HRMS for $C_{21}H_{20}O$: calc : 288,1514; found : 288,1506.

1,3-Diphenyl-5-methyl-2-vinylhexa-3,4-dien-1-one **6**

^1H NMR (ppm) : 1.27 (s, 3H); 1.62 (s, 3H); 5.05 (d, J = 7.5 Hz, 1H); 5.30 (d, J = 16.5 Hz), 5.32 (d, J = 11 Hz); 6.19 (ddd, J = 16.5 Hz, 11 Hz, 7.5 Hz); 7.18-7.62 (m, 8H); 7.87-8.02 (m, 2H).

^{13}C NMR (ppm) : 18.5, 19.9, 53.4, 101.2, 102.5, 117.9, 126.2, 126.5, 128.3, 128.5, 128.6, 132.6, 135.6, 136.2, 197.8, 203.9.

Carbonic acid (3-methyl-1-phenylbut-1-yn-3-yl) ester (cyclohexa-1,3-dien-1-yl) ester **1l**

IR (cm^{-1}) : 2 230, 1 763, 1 597, 1 491, 1 384, 1 366.

^1H NMR (ppm) : 1.83 (s, 6H); 2.36-2.45 (m, 4H); 5.64 (bd, $J \approx$ 9 Hz, 1H); 5.75 (bd, J = 5 Hz, 1H); 5.86 (dd, J = 9 Hz, 5 Hz, 1H); 7.24-7.36 (m, 3H); 7.38-7.50 (m, 2H).

^{13}C NMR (ppm) : 23.8, 25.0, 28.8, 75.6, 84.8, 88.9, 110.5, 122.3, 122.7, 123.5, 128.2, 128.5, 131.8, 150,5.

MS : m/z = 238, 160, 143.

HRMS for $C_{17}H_{18}O$: calc : 238,1358; found : 238,1353.

4-(3-Methyl-1-phenylbuta-1,2-dien-1-yl)cyclohex-2-en-1-one **2l**

IR (cm^{-1}) : 1 952, 1 681, 1 384, 1 362.

^1H NMR (ppm) : 1.80 (d, J = 4 Hz, 6H); 1.88-2.12 (m, 1H); 2.22-2.36 (m, 1H); 2.36-2.67 (m, 2H); 3.67 (m, 1H); 6.03 (dd, J = 10 Hz, 2 Hz, 1H); 6.93 (dd, J = 10 Hz, 3 Hz, 1H); 7.18-7.42 (m, 5H).

^{13}C NMR (ppm) : 20.3, 20.4, 28.4, 36.4, 36.6, 100.7, 104.7, 126.3, 126.7, 128.5, 129.0, 136.5, 152.7, 199.7, 202.3.

MS : m/z = 238, 182, 167, 143.

HRMS for $C_{17}H_{18}O$: calc : 238,1358; found : 238,1353.

Carbonic acid (3-methyl-1-phenylbut-1-yn-3-yl) ester (hexa-1,3,5-trien-1-yl) ester **1m**

Mixture of Z/E = 45:55 stereomer for the C_1 enol ether double bond.

IR (cm^{-1}) : 2 230, 1 766, 1 650, 1 625, 1 255, 1 177, 1 004; 960, 875.

^1H NMR (ppm) : 6.00-6.58 (m, 3H); 7.22-7.48 (m, 5H). Z isomer : 1.85 (s, 2.7H); 5.08 (bd, $J \approx$ 10 Hz); 5.20 (d, J = 16 Hz); 5.32 (dd, J = 10.5 Hz, 6 Hz, 0.45H); 6.61 (dd, J = 15 Hz, 10.5 Hz, 0.45H); 6.93 (d, J = 6 Hz, 0.45H); 6.93 (d, J = 6 Hz, 0.45H). E isomer : 1.83 (s, 3.3H); 5.13 (d, $J \approx$ 10 Hz); 5.25 (d, J = 16 Hz).

^{13}C NMR (ppm) : 28.80, 28.83, 76.02, 76.10, 85.10, 88.74, 112.49, 115.25, 117.04, 117.98, 122.14, 122.16, 124.73, 127.30, 128.19, 128.61, 131.84, 133.29, 135.69, 136.70, 139.98, 150.02, 150.09.

MS : m/z = 238, 160, 143.

HRMS for $C_{17}H_{18}O$: calc : 238,1358; found : 238,1353.

7,7-Dimethyl-9-phenylnona-2,4-dien-8-ynal **3m**

Mixture of Z/E = 75:25 stereomer for the C4-double bond.

IR (cm^{-1}) : 2 810, 2 720, 2 231, 1 683, 1 635, 990, 962.

^1H NMR (ppm) : 6.40-6.55 (m, 1,25H); 7.22-7.40 (m, 5H). Z isomer : 1.36 (s, 4.5H); 2.55 (dd; J = 8 Hz, 1 Hz, 1.5H); 6.18 (dd, J = 15 Hz, 8 Hz); 6.28 (dd, J = 10 Hz, 8 Hz); 7.48 (dd, J = 15 Hz, 11 Hz, 0,7H); 9.59 (d, J = 8 Hz, 0.75H). E isomer : 1.32 (s, 1.5 Hz); 2.41 (d, J = 6 Hz, 0.50H); 6.11 (dd, J = 15 Hz, 8 Hz); 7.16 (dd, J = 10 Hz, 5 Hz); 9.56 (d, J = 8 Hz, 0.25H).

^{13}C NMR (ppm) : 29.0 , 32.0, 81.5, 95.7, 123.1, 128.1, 128.3, 131.5, 194.0, 194.2.

MS : m/z = 238, 223, 143.

2-(3-Methyl-1-phenylbut-1-yn-3-yl)hexa-3,5-dienal **7**

Single Z stereomer.

IR (cm^{-1}) : 2 820, 2 723, 2 228, 1 724, 1 642, 1 000, 915, 653.

^1H NMR (ppm) : 1.30 (s, 3H); 1.39 (s, 3H); 3.28 (dd, J = 10 Hz, 4 Hz, 1H); 5.26 (bd, $J \approx$ 11 Hz, 1H); 5.34 (bd, $J \approx$ 16 Hz, 1H); 5.74 (dd, J = 11 Hz, 10 Hz, 1H); 6.38 (dd, J = 11 Hz, 10 Hz, 1H); 6.58 (ddd, J = 16 Hz, 11 Hz, 10 Hz, 1H); 7.30-7.45 (m, 5H); 9.78 (d, J = 4 Hz, 1H).

^{13}C NMR (ppm) : 27.5, 28.3, 33.3, 60.5, 83.5, 93.1, 120.7, 123.0, 123.1, 128.1, 128.3, 131.6, 131.7, 135.0, 200.5.

MS : m/z = 238, 223, 143.

HRMS for $C_{17}H_{18}O$: calc : 238,1358; found : 238,1360.

9-Methyl-7-phenyldodeca-2,4,7,8-tetraenal **2m**

Mixture of three stereomers (70% of the E-E).

IR (cm^{-1}) : 1 953, 1 683, 1 640, 1 598, 760, 695.

^1H NMR (ppm) : E-E isomer : 1.81 (s, 4.2H); 3.32 (d, $J \approx$ 6 Hz, 1.4H); 6.08 (dd, J = 15 Hz, 8 Hz, 0.7H); 6.34-6.48 (m, 1.4H); 7.10 (dd, J = 15 Hz, 10 Hz, 0.7H); 7.10-7.40 (m, 5H); 9.53 (d, J = 8 Hz, 0.74H).

^{13}C NMR (ppm) : 20.3, 34.4, 99.3, 100.7, 125.8, 126.4, 128.3, 129.4, 130.4, 137.1, 144.1, 152.2, 193.7, 202.3.

MS : m/z = 238, 223, 209, 143.

HRMS for $C_{17}H_{18}O$: calc : 238,1358; found : 238,1353.

Carbonic acid (3-methyl-1-phenylbut-1-yn-3-yl) ester (prop-2-en-2-yl) ester **1n**

IR (cm^{-1}) : 2 230, 1 763, 1 678, 1 384, 1 366, 1 217, 1 124, 894, 758, 692.

^1H NMR (ppm) : 1.83 (s, 6H); 1.99 (s, 3H); 4.70 (m, 1H); 4.84 (m, 1H); 7.24-7.49 (m, 5H).

^{13}C NMR (ppm) : 19.2, 28.8, 75.4, 84.8, 89.1, 101.7, 122.4, 128.2, 128.5, 131.8, 150.5, 152.8.

MS : m/z = 244, 204, 143.

HRMS for $C_{15}H_{16}O_3$: calc : 244,1099; found : 244,1104.

6-Methyl-4-phenylhepta-4,5-dien-2-one **2n**

IR (cm^{-1}) : 1 954, 1 714, 1 356, 756, 690.

^1H NMR (ppm) : 1.85 (s, 3H); 2.20 (s, 3H); 3.45 (s, 2H); 7.15-7.35 (m, 5H).

^{13}C NMR (ppm) : 20.0, 28.6, 97.9, 99.0, 125.9, 126.6, 128.5, 137.0, 203.3, 207.6.

MS : m/z = 200, 185, 143, 43.

HRMS for $C_{14}H_{16}O$: calc : 200,1201; found : 200,1198.

4-Methyl-2-phenylbut-1-en-3-yne **4n**

IR (cm^{-1}) : 2 210, 1 613, 898, 756, 690.

^1H NMR (ppm) : 1.99 (dd, $J \approx 1$ Hz, 3H); 5.30 (m, 1H); 5.40 (m, 1H); 7.25-7.50 (m, 5H).

^{13}C NMR (ppm) : 23.5, 88.4, 90.6, 121.9, 123.3, 126.9, 128.1, 128.3, 131.6.

MS : m/z = 142, 141, 127.

HRMS for $C_{11}H_{10}$: calc : 142,0783; found : 142,0781.

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