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Reactivity of Substituted and Unsubstituted Diphenylphosphonium Diylides Towards Carbonic Acids Derivatives.

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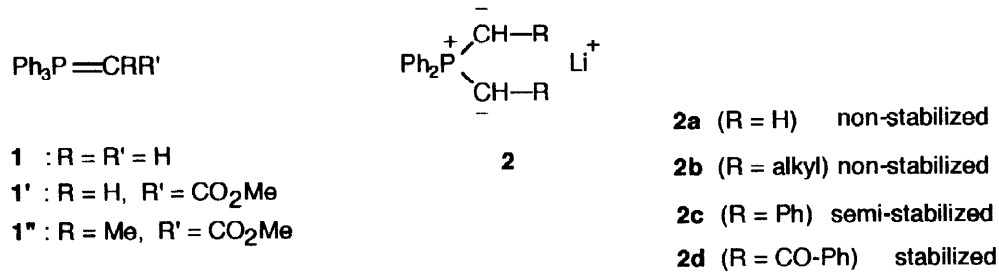
Abstract : In order to further delimit the scope of application of diphenylphosphonium diylides, their reactivity towards carbonic acid derivatives was investigated. Non-stabilized diylides react with ethyl carbonate to give new monoylide intermediates which lead, by *in situ* Wittig reaction with carbonyl compounds, to the synthesis of α,β-unsaturated esters or acids the double bond being di- or trisubstituted. The reaction proceeds in mild conditions and with high *E* stereoselectivity. Stabilized diylides are inactive towards carbonates but semi-stabilized diylides react with ethyl carbonate leading to the synthesis of non-functionalized alkenes instead of the α,β-unsaturated esters or acids.

INTRODUCTION

In our recent work, it has been shown that the non-substituted and non-stabilized diphenylphosphonium diylide **2a**, more reactive, owing to its reinforced carbanionic activity, than the corresponding phosphonium monoylide **1**, constitutes an excellent tool in organic synthesis.[1] Presently we are trying to enlarge our results to substituted diylides **2b-2d** (non-stabilized **2b**, semi-stabilized **2c** or stabilized **2d**) in order to determine the limitations of the synthetic application field for this family of reagents.



Scheme 1

Recently, we showed that the non-stabilized and non-substituted diylide **2a** reacts with a cyclic carbonate enabling, in a ponctual case, the synthesis of a functionalized α,β-unsaturated ester.[2] We present here a more general work concerning the reactivity of non-substituted and substituted diylides **2a-d** towards

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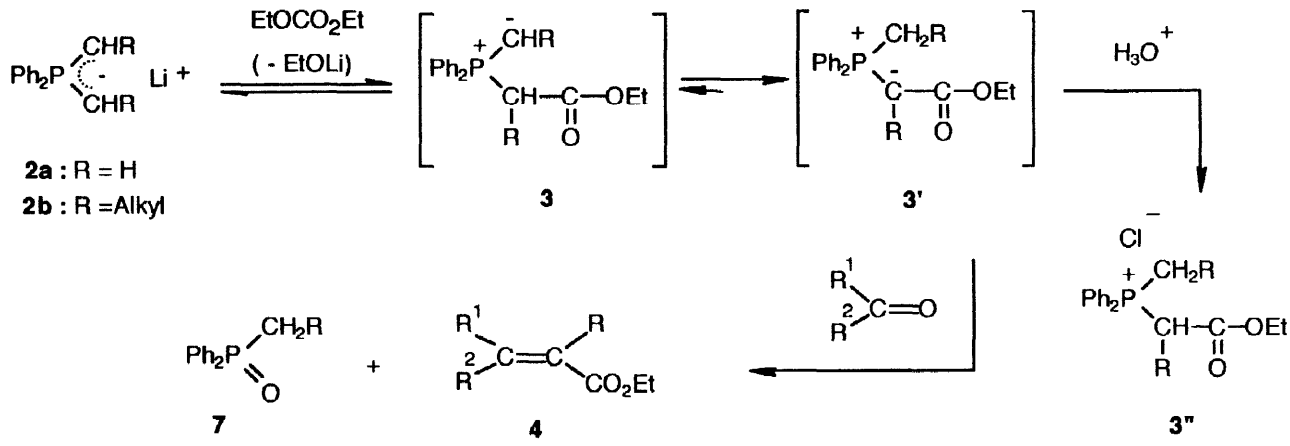
derivatives of carbonic acid. The study, essentially undertaken with the ethyl carbonate, allowed us to realize the synthesis of α,β-unsaturated esters, the double bond being di- or trisubstituted, as well as the synthesis of corresponding carboxylic acids, with good yields and high stereoselectivity, in short times and under very mild conditions. Further this reaction constitutes a good model to delimitate, depending on their stabilization degree, the scope and limitations in the use of phosphonium diylides.

RESULTS AND DISCUSSION

The non-stabilized diylide **2a** (**a** : R = H) reacts with ethyl carbonate to give the corresponding intermediate monoylide **3a** (Scheme 2). The latter, through an intramolecular prototropy, is transformed into a new monoylide **3'a**, exhibiting a stabilized character owing to the presence of an ester group on the carbanion. This monoylide reacts *in situ* with aldehydes to give α,β-unsaturated esters **4** with a disubstituted double bond (table 1, Scheme 2), together with methyldiphenylphosphine oxide **7a**. The corresponding acids **5** are obtained quantitatively through direct basic hydrolysis of the reaction mixture (table 3, Scheme 5). It is noteworthy that the protonation of this mixture, before adding the carbonyl compound, quantitatively leads to the phosphonium salt **3"a**, in good accordance with the formation of the intermediate monoylides **3a** and **3'a**.

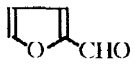
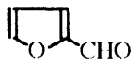
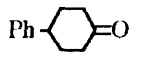
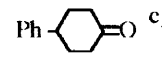


Scheme 2

In presence of non enolisable aldehydes (benzaldehyde, furfuraldehyde, cinnamaldehyde) or enolisable ones (3-methyl-3-phenylpropanal), excellent yields (88-95%) of α,β-unsaturated esters (respectively **4e, 4g, 4i** and **4k**) are obtained in a very short time, the *Wittig* reaction with **3'a** being almost instantaneous (less than 10 minutes at 20°C). These results, obtained through the monoylide **3'a** (R = H) as Wittig reagent in the last step, are very interesting with reference to the literature. Indeed, in comparison, the synthesis of α,β-unsaturated esters from aldehydes and the related stabilized monoylide, the triphenylcarbethoxymethylene phosphorane **1'**, needs longer reaction times and gives lower yields [3a, 4] : several days at room temperature for the synthesis of ethyl cinnamate from benzaldehyde (77% yield) [5a], or several hours in refluxing benzene for furfuraldehyde or enolisable aldehydes (yield 50%).[5b] Even the reaction beetween **3'a** (prepared from the beforehand isolated corresponding phosphonium salt) and benzaldehyde, realized in different solvent/base systems gives in the best case lower results.[5c] Only a very recent example deals with the synthesis of ethyl cinnamate and immediate analogs through a Wittig reaction from **1'** and aromatic aldehydes, with good yields and short

reaction times (10 mn).[4] The technique used to obtain these results, i.e. the irradiation with microwaves, could however limit the interest of the method.

Table 1 : Synthesis of α,β-Unsaturated Esters **4** or Alkenes **6**, by Reaction of Diylides **2a** (R = H), **2b** (R = alkyl) or **2c** (R = phenyl), with Ethyl Carbonate ($EtOCO_2Et$), Followed by Addition of Aldehydes or Ketones (Scheme 3).

Entry	Diylides **2** R	R^1 \ R^2 C=O	Alkenes **6** Yields (%) [a]	(E / Z)	Ester **4** Yields (%) [a]	(E / Z) [b]
1	H	Ph-CHO	-		**4e** 95	95 / 5
2	Me	Ph-CHO	-		**4f** 85	80 / 20
3	H		-		**4g** 95	95 / 5
4	Me		-		**4h** 80	81 / 19
5	H	Ph-CH=CH-CHO	-		**4i** 95	92 / 8
6	Me	Ph-CH=CH-CHO	-		**4j** 92	75 / 25
7	H	Ph-CH(CH_3)CH_2-CHO	-		**4k** 88	95 / 5
8	Me	Ph-CH(CH_3)CH_2-CHO	-		**4l** 70	68 / 32
9	H		-		**4m** 70	-
10	Me	 [c]	-		**4n** 40	-
11	H	Ph-CO-Ph	-		0	-
12	Ph	Ph-CHO	**6o** 75	100 / 0	0	-
13	Ph	O_2N-C_6H_4-CHO	**6p** 85	100 / 0	0	-
14	-COPh	Ph-CHO	0		0	-

[a] Isolated yield. [b] Determined by ^{1}H-NMR, GC/MS. [c] In addition to **4n** we observe the formation of the 2-(4-phenylcyclohexylidene)-4-phenylcyclohexanone (autocondensation of phenylcyclohexanone : identified by GC/MS).

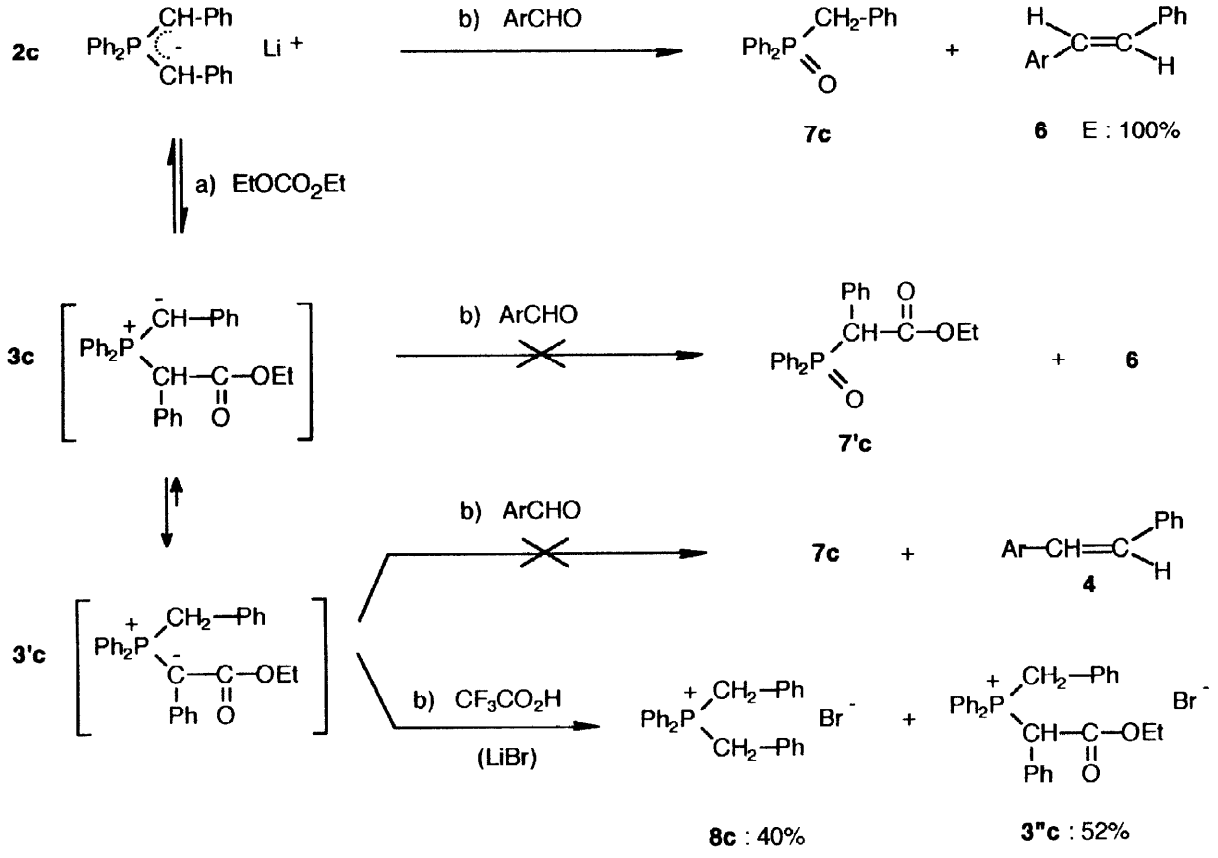
Our synthetic way, *via* the monoylides **3'**, corresponds then to a progress in this field. In comparison with **1'**, the improvement probably results from the change of a phenyl group by a methyl, which increases the electronic density on the phosphorus, exalting thus the carbanionic activity of the corresponding monoylides.[3b, 6] However, the extent of the observed phenomenon does not correspond to the related examples already described in the litterature. Indeed, the change of phenyl substituents on the phosphonium cation by alkyl ones is known to increase the speed of the Wittig reaction [3c, 7], but the phenomenon is not very marked, particularly in the case of stabilized ylides. The outcome of such substituents exchanges concern rather the stereochemistry of the reaction.[3c]

The non-stabilized diylide **2a** permits even from enolisable ketones the formation of α,β-unsaturated esters with a disubstituted double bond (**4m**), but under more drastic experimental conditions than from the

aldehydes (2 days in refluxing THF : benzophenone does not react). Nevertheless, our system presents interesting performances compared to the most reported results in the literature for this type of Wittig reaction. Indeed, as well the triphenylphosphorane **1'** as the related stabilized mono-, di- or trialkyl phosphoranes [$Ph_nR_{3-n}P{=}CHCO_2R'$ (n = 0, 1, 2) ; R' = Me, Et] react scarcely or not at all with ketones, except in drastic conditions.[3a, 8] The only example with performances comparable to diylide **2a** involves a carbo-*tert*-butoxymethylene triphenylphosphonium monoylide and a pyrrolidone as a ketone.[8e]

The substituted non-stabilized diylide **2b** (**b** : R = Me) enables also the synthesis of α,β-unsaturated esters, in the same way as **2a**, through the *in situ* formation of a diphenylethylphosphonium monoylide intermediate **3'b**, carrying this time two substituents on the carbanion (an alkyl group and an ester function). From non enolisable or enolisable aldehydes, excellent yields of α,β-unsaturated esters, with trisubstituted double bond, are thus obtained and, as previously, within a very short time (table 1 : esters **4f**, **4h**, **4j** and **4l**). On the other hand, starting from phenylcyclohexanone, the corresponding ester **4n** is obtained in moderate yield (40%) together with the formation of 2-(-4-phenylcyclohexylidene)-4-phenylcyclohexanone : this last product which was surprisingly not observed in the same reaction starting from **2a**, could result from an aldol condensation initiated by the presence of lithium ethanolate. However when, in order to neutralize this base, one equivalent of benzoïc acid was added before the phenylcyclohexanone in the reaction mixture, no improvement was observed.

The semi-stabilized diylide **2c** (**c** : R = Ph) reacts with ethyl carbonate to give the corresponding monoylide intermediates **3c** and **3'c** (Scheme 3).



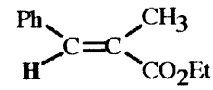
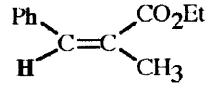
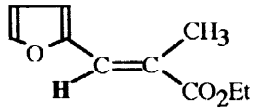
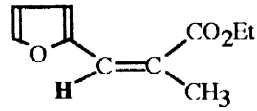
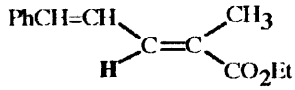
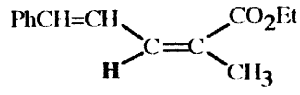
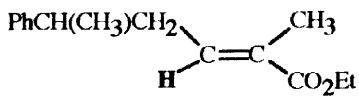
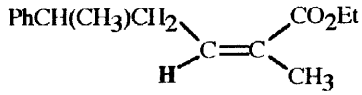
Scheme 3

This reactivity is pointed out by the total disappearance of the ^{31}P-NMR signal of the starting diylide in favour of two peaks probably corresponding to the rotamers of **3'c**. [9] Their existence is also demonstrated by the formation of the phosphonium salts **3"c** and **8c**, isolated with yields of 52% and 40% respectively by protonation of the reaction mixture. The carbanion **3'c** twice stabilized by the ester and phenyl groups is however inactive towards aldehydes. The product obtained is the alkene **6** (table 1 : entries 12-13 ; yield 75-85% ; E/Z = 100/0), which results from a Wittig reaction of aldehydes with the intermediate monoylide **3c** or directly with the starting diylide **2c**, these two ways involving a displacement of equilibrium. The second hypothesis however seems to be the most likely because the benzyldiphenylphosphine oxide **7c** is the only product observed *in situ* and isolated together with the alkenes **6**. The carbethoxybenzyldiphenylphosphine oxide **7'c** which would result from a Wittig reaction with the intermediate monoylide **3c** has never been observed.

Last, the stabilized diylide **2d** (**d** : R = COPh) is inactive towards carbonates. The ^{31}P-NMR signal of the starting diylide is unchanged in the presence of ethyl or phenyl carbonate, the protonation of the mixture leading to the quantitative recovery of the initial phosphonium salt **8d** $[Ph_2P(CH_2COPh)_2]^+ Cl^-$.

Concerning the stereochemistry of the α,β-unsaturated esters, the results show a good *E* stereoselectivity. The determination of the structure has been realized by ^{1}H-NMR spectroscopy, from the $^3J_{H,H}$ coupling constants, whenever possible. For α,β-unsaturated esters with trisubstituted double bond the determination has been realized from the chemical shift of the proton carried by the carbon β to the ester function, which presents a very characteristic deshielding when the configuration is *trans*. [10]

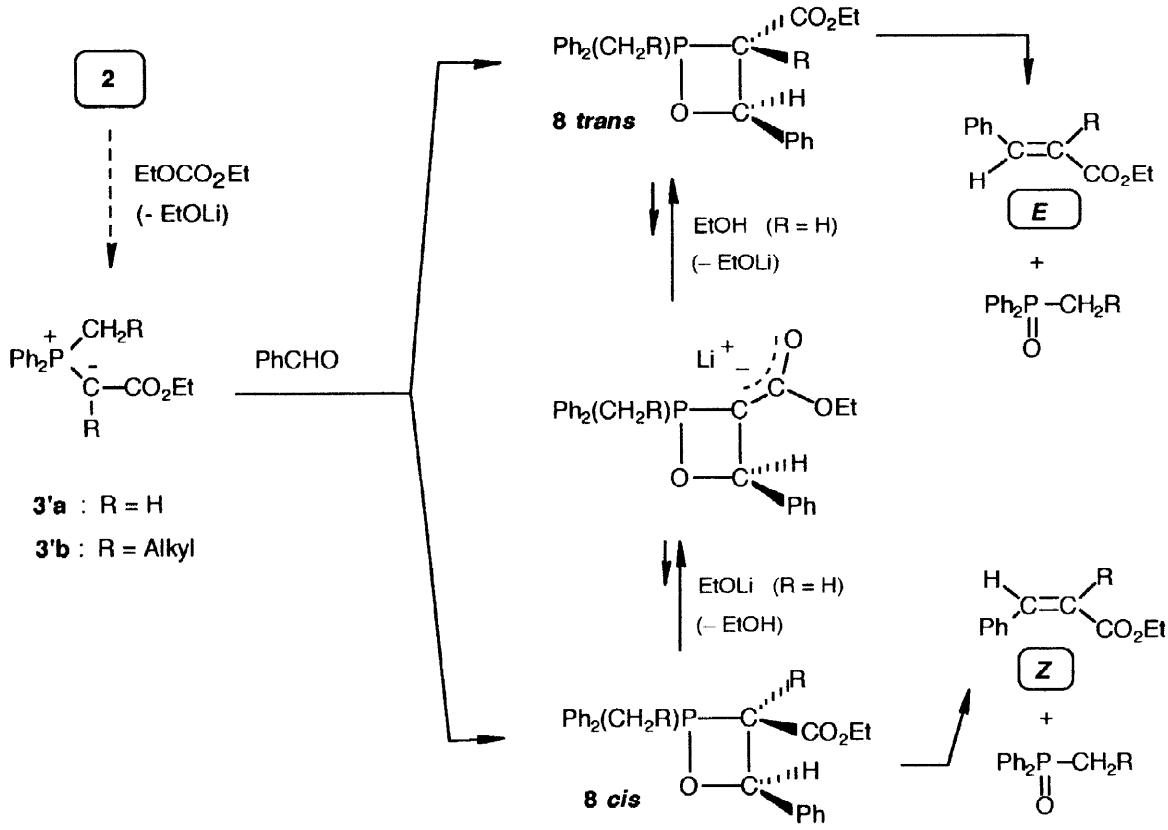
Table 2 : Identification of ***E*** and ***Z*** Isomers for α,β-Unsaturated Esters with Trisubstituted Double Bond. Chemical Shift of the Proton Carried by the Carbon β to the Ester Function.

ester	isomer *E*	δ (H) / (ppm)	isomer *Z*	δ (H) / (ppm)
4f		7.72		6.71
4h		7.42		6.45
4j		7.50-7.29		6.60
4l		6.77		5.85

These results are in accordance with the *E* stereoselectivity expected for the Wittig reaction from stabilized phosphonium monoylides. [3d] Notice that, starting from **2a** which is transformed into the stabilized methyldiphenylphosphonium monoylide **3'a** as Wittig reagent, the *E/Z* ratio is greater (95/5) than the 85/15 ratio usually observed in the Wittig reaction from the related stabilized triphenylphosphonium monoylides **1'** and aldehydes. [3c, 5a, 11] If this improvement has already been noted when the three phenyl groups of **1'** are

replaced by three cyclohexyl or three *n*butyl groups or by one ferrocenyl, [3c, 7c, 11, 12] the opposite phenomenon has also been observed.[5c] Some correlations link these modifications to steric factors, an increase of the substituent size on the phosphorus atom promoting the *E* isomer formation.[13] Other litterature results, more contrasted, show that this increase has a little effect on the stereochemistry of the reaction.[12] According to our results, it seems on the contrary that a higher steric hindrance on the phosphorus favours rather the *Z* isomer, the *E* form remaining the major one : starting from diylide **2b** (R = Me), the *E*/*Z* ratio falls around 80/20 (table 1).

To explain the different stereochemical results obtained from **2a** and **2b**, the *in situ* generation of lithium ethanolate in our reaction mixture could probably be taken into account (Scheme 4).



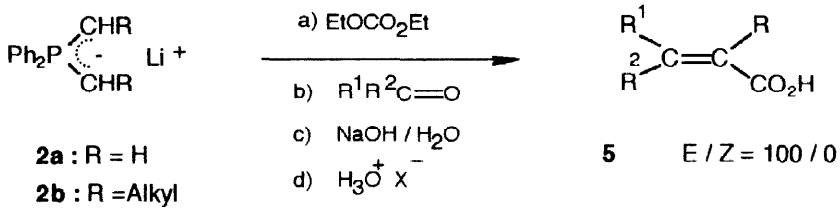
Scheme 4

Indeed, the probable *Wittig* reaction mechanism, [5c] applied to the stabilized monoylides **3'** intermediate, involves a first irreversible step, slow and under kinetic control, leading to the formation of an oxaphosphetane **8** (Scheme 4). In this step, the later transition state close to the products, leads preferentially to the *trans* oxaphosphetane and further to the *E* α,β-unsaturated ester. The formation of the *cis* oxaphosphetane, not favoured, is however not negligible since the *E*/*Z* α,β-unsaturated ester ratio found in the case of **2b** is around 80/20. To explain, starting from **2a** (R = H) the increase of the *E* isomer ratio (E/Z : 95/5), we can postulate that in this case the oxaphosphetane *cis* is probably isomerized by EtOLi into the thermodynamically more stable oxaphosphetane *trans*. Starting from diylide **2b** (R = alkyl) the increase of the

E isomer ratio is not observed since in this case the isomerization of the oxaphosphetane *cis* (R ≠ H) is not posible. Such basic isomerization, known as the Schlosser modification in the case of non stabilized monoylides and with strong basis, can be here taken into account, owing to the presence of the ester function which acidifies the vicinal proton, on the oxaphosphetane ring (scheme 4).

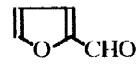
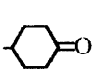
Last, it is noteworthy that most of the stereochemical studies reported in the literature were done with reaction times higher than four hours, without specification of the possible influence of the reaction mixture on an eventual isomerization, subsequent to the α,β-unsaturated ester formation. [3e, 14] Our measurements, very quickly realized, could be on this point of view more significant.

As an extension of the ester synthesis it was possible, starting from substituted or non-substituted diylides (**2a-2b**), to obtain directly the corresponding α,β-unsaturated acids by the *in situ* saponification of the reaction mixtures (Scheme 5 ; table 3). The acids have been obtained with good yields and a total *E* stereochemistry except in the case of terephthalaldehyde.



Scheme 5

Table 3 : Synthesis of α,β-Unsaturated Acids **5** by Reaction of Diylides **2a** (R = H) or **2b** (R = methyl, ethyl) with Ethyl Carbonates ($EtOCO_2Et$), Followed by Addition of Aldehydes or Ketones and then by Basic Hydrolysis of the Reaction Mixture.

Entry	Diylides **2** R	R^1 / R^2 C=O	Acid **5**	Yields (%) [a]	(E / Z)
16	H	PhCHO	**5e**	92	100 / 0
17	Me	PhCHO	**5f**	62	100 / 0
18	Et	PhCHO	**5r**	57	100 / 0
19	H	O_2N-C_6H_4-CHO	**5s**	95	100 / 0
20	H		**5g**	84	100 / 0
21	H	Ph-CH=CH-CHO	**5i**	79	100 / 0
22	H	Ph-$(CH_2)_2$-CHO	**5t**	90	100 / 0
23	H	Ph- 	**5m**	55	-
24	H	OHC-C_6H_4-CHO	**5u**	50	b)

[a] Isolated yield . [b] Presence of three isomers *EE / EZ / ZZ* which have not been separated.

An interesting feature of this method lies in the fact that the generation of the acid is possible *in situ* after several synthetic operations using the ester function as protecting group. Related studies from the stabilized phosphonium monoylide **1'** have been realized, but they require more drastic conditions (as already seen for the esters synthesis) and essentially concern the synthesis of α,β-unsaturated acids with a disubstituted double bond. Moreover, at least in the case of aldehydes [6, 5b], the stereochemical aspect has not been considered.

CONCLUSION

The study of the reactivity of phosphonium diylides **2** towards carbonic acid derivatives confirms, widening their application field, that these reagents are good tools in organic synthesis.

Thus non-stabilized phosphonium diylides **2a** (R = H) and **2b** (R = Me, Et) react with ethyl carbonate allowing, in presence of carbonyl compounds, the synthesis of α,β-unsaturated esters **4** with a di- or trisubstituted double bond. The reaction proceeds in very mild conditions (very short time at room temperature) and with a high *E* stereoselectivity, particularly starting from **2a**. The corresponding *E* acids are obtained in similar conditions with an *in situ* additional hydrolysis step of the reaction mixture.

The semi-stabilized diylides **2c** (R = Ph) react also with ethyl carbonate but the resulting intermediate monoylide **3'c**, twice stabilized by the ester function and by the phenyl group, does not react with carbonyl compounds. The products obtained, the *E* alkenes, result from the direct *Wittig* reaction with the starting diylide **2c** which is in equilibrium with **3 c** and **3'c**.

Last, the stabilized diylide **2d** (R = COPh) is inactive towards ethyl or phenyl carbonates.

EXPERIMENTAL

All experiments were performed under nitrogen by means of the Schlenk technology. NMR spectra were recorded on a Brucker AC 200 instrument (at 50.32 MHz for ^{13}C-NMR and 200.13 MHz for ^{1}H-NMR). The chemical shifts are expressed in parts per million (ppm) downfield from external tetramethylsilane. Coupling constants (*J*) are given in Hertz. Multiplicities are recorded as s (singlet), d (doublet), t (triplet), td (triplet of doublet), tq (triplet of quartet), q (quartet) and m (multiplet). Infrared spectra were obtained on a Nicolet 205 FT-IR Spectrometer, wavelength are given in cm^{-1}. Mass spectra were obtained on a JEOL JMS-DX 300 *via* direct introduction by positive Electronic Impact (EI+)(70 eV). Microanalyses were performed by the Microanalysis Laboratory at ENSCM. Melting points were carried out on a METTLER FP 5 or a LEITZ 350 apparatus, for recrystallized products. Tetrahydrofuran (THF) was distilled under nitrogen atmosphere over sodium/benzophenone and stored upon sodium.

General procedure for the synthesis of α,β-unsaturated esters (4) and alkenes (6).

Under nitrogen atmosphere, the phosphonium salt [16] (10 mmol) corresponding to the wished diylide [**2a** (R = H), **2b** (R = Me), **2c** (R = Ph) or **2d** (R = COPh)], is introduced in anhydrous THF (100 ml). To the heterogeneous mixture, cooled at -50 °C, a solution of *n*-butyllithium 2.5 N in hexane (8 ml, 20 mmol) is added dropwise. After 30 mn at this temperature, the solution is allowed to warm up to room temperature.

Then, 10 mmol of ethyl carbonate in the case of diylides **2a**, **2b** and **2c** or 10 mmol of ethyl or phenyl carbonate in the case of the diylide **2d**, are respectively added to the reaction mixture. After 15 minutes at room temperature, the carbonyl compound (20 mmol) is then added quickly, except in the case of **2d** for which no reaction with carbonates is observed.

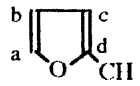
From **2a** or **2b** and enolisable or non enolisable aldehydes, the reaction is performed almost instantaneously, in less than 10 minutes at 20°C (**4e**, **4g**, **4i**, **4k** and **4f**, **4h**, **4j**, **4l**). From **2a** or **2b** and phenylcyclohexanone, the reaction is stopped after two days in refluxing THF (**4m** and **4n**), and from **2c** and non enolisable aldehydes, the reaction is performed in 3 hours in refluxing THF (**6o** and **6p**).

Then, in all the cases, the mixture is acidified with HCl 0.2 N (100 ml). After evaporation of solvent, extraction with CH_2Cl_2 (3 x 100ml), washing of the organic layer with water and drying over Na_2SO_4, the mixture is concentrated and turns into a crude oil, which is purified by chromatography on silica gel to give α,β-unsaturated esters **4** or alkenes **6**.

Ethyl cinnamate **4e** : ***E isomer*** [4]. IR (KBr) (cm^{-1}) : ν = 3045, 2970, 1700 (CO), 1632, 1460, 1315, 1260, 1170 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.68 (d, $^3J_{H,H}$ = 16.03 Hz, 1H, C*H*=CH-CO),7.52-7.33 (m, 5H, C_6H_5), 6.43 (d, $^3J_{H,H}$ = 16.03 Hz, 1H, CH=C*H*-CO), 4.25 (q, $^3J_{H,H}$ = 7.13 Hz, 2H, CH_3CH_2O), 1.32 (t, $^3J_{H,H}$ = 7.13 Hz, 3H, CH_3CH_2O). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 166.9 (*C*O), 144.6 (*C*=C-CO), 134.5 (*i-C*, C_6H_5), 130.2 (*p-C*, C_6H_5), 128.9 (*m-C*, C_6H_5), 128 (*o-C*, C_6H_5), 118.3 (C=*C*-CO), 60 (CH_2CH_3), 14.3 (CH_2CH_3). MS (EI) : *m / z* (%) 176 (M^+, 35), 148 (22), 131 (100), 103 (50), 77 (35). Anal. Calcd. for $C_{11}H_{12}O_2$: H, 6.87 ; C, 74.96 ; O, 18.17. Found : H, 6.75 ; C, 74.88 ; O, 17.86.

Ethyl 2-methyl-cinnamate **4f** : ***E isomer*** [15a]. IR (KBr) (cm^{-1}) : ν = 3050, 2970, 1705 (CO), 1632, 1442, 1312, 1250, 1110 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.72 (q, $^4J_{CH_3,H}$ = 1.47 Hz, 1H, C*H*=C-CH_3), 7.42-7.28 (m, 5H, C_6H_5), 4.28 (q, $^3J_{H,H}$ = 7.12 Hz, 2H, CH_3CH_2O), 2.12 (d, $^4J_{CH_3,H}$ = 1.47 Hz, 3H, CH=C-C*H*$_3$), 1.35 (t, $^3J_{H,H}$ = 7.12 Hz, 3H, CH_3CH_2O). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 168.7 (*C*O), 138.63 (*C*=C-CO), 135.99 (*i-C*, C_6H_5), 129.62, 128.35, 128.23 (*o-C*, *m-C*, *p-C*, C_6H_5), 128.7 (C=*C*-CO), 60.86 (CH_2CH_3), 14.33 (CH_2CH_3), 14.04 (C=C-*C*H$_3$). MS (EI) : *m / z* (%) 190 (M^+, 55), 161 (20), 145 (55), 117 (100). Anal. Calcd. for $C_{12}H_{14}O_2$: H, 7.42 ; C, 75.75 ; O, 16.83. Found : H, 7.27 ; C, 75.89 ; O, 17.11.

Z isomer [15b]. ^{1}H-NMR ($CDCl_3$) : δ = 7.38-7.26 (m, 5H, C_6H_5), 6.71 (q, $^4J_{CH_3,H}$ = 1.64 Hz, 1H, C*H*=C-CH_3), 4.12 (q, $^3J_{H,H}$ = 7.12 Hz, 2H, CH_3CH_2O), 2.10 (d, $^4J_{CH_3,H}$ = 1.64 Hz, 3H, CH=C-C*H*$_3$), 1.11 (t, $^3J_{H,H}$ = 7.12 Hz, 3H, CH_3CH_2O). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 168.9 (*C*O), 134.27 (C=C-CO), 136.40 (*i-C*, C_6H_5), 128.09, 127.99, 127.52 (*o-C*, *m-C*, *p-C*, C_6H_5), 130.20 (C=*C*-CO), 60.57 (CH_2CH_3), 13.77 (CH_2CH_3), 21.04 (C=C-*C*H$_3$).

Ethyl 3-(2-furyl)-acrylate **4g** 

E isomer [15c] IR (KBr) (cm^{-1}) : ν = 3140, 2965, 1715 (CO), 1630, 1460, 1255 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.44 (d, $^3J_{Ha,Hb}$ = 1.8 Hz, 1H, *Ha*), 7.39 (d, $^3J_{H,H}$ = 15.6 Hz, 1H, C*H*=CH-CO), 6.56 (d, $^3J_{Hc,Hb}$ = 3.38 Hz, 1H, *Hc*), 6.42 (dd, $^3J_{Hb,Hc}$ = 3.37 Hz, $^3J_{Hb,Ha}$ = 1.8 Hz, 1H, *Hb*), 6.27 (d, $^3J_{H,H}$ =15.7 Hz, 1H, CH=C*H*-CO), 4.16 (q, $^3J_{H,H}$ = 7.13 Hz, 2H, CH_3CH_2O), 1.28 (t, $^3J_{H,H}$ = 7.13 Hz, 3H, CH_3CH_2O). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ =

166.90 (*C*O), 150.90 (*C*$_d$), 144.64 (*C*$_a$), 130.90 (*C*=C-CO), 114.58 (C=*C*-CO), 115.90-112.20 (*C*$_c$, *C*$_b$), 60.34 (*C*H$_2$CH$_3$), 14.24 (CH$_2$*C*H$_3$). MS (EI) : *m / z* (%) 166 (M^+, 70), 138 (53), 121 (100). Anal. Calcd. for $C_9H_{10}O_3$: H, 6.07 ; C, 65.04 ; O, 28.90. Found : H, 6.21 ; C, 64.83 ; O, 28.35.

E* + *Z* *isomer (mixture). ^{1}H-NMR ($CDCl_3$) : identification of the Z isomer (by comparison with the spectra of the isolated *E* isomer) : δ = 7.62 (d, $^3J_{Ha,Hb}$ = 1.85 Hz, 1H, *H*$_a$), 6.80 (d, $^3J_{H,H}$ = 12.1 Hz, 1H, C*H*=CH-CO), 6.56 (d, 1H, *H*$_c$), 6.46 (dd, $^3J_{Hb,Hc}$ = 3.4 Hz, $^3J_{Hb,Ha}$ = 1.85 Hz, 1H, *H*$_b$), 5.7 (d, $^3J_{H,H}$ =12.1 Hz, 1H, CH=C*H*-CO), 4.14 (q, $^3J_{H,H}$ = 7.12 Hz, 2H, CH$_3$C*H*$_2$O), 1.26 (t, $^3J_{H,H}$ = 7.12 Hz, 3H, *C*H$_3$CH$_2$O). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 166.90 (*C*O), 151 (*C*$_d$), 144.52 (*C*$_a$), 130.34 (*C*=C-CO), 114.32 (C=*C*-CO), 117-112.55 (*C*$_c$, *C*$_b$), 60.06 (*C*H$_2$CH$_3$), 14.24 (CH$_2$*C*H$_3$).

<u>*Ethyl 3-(2-furyl)-2-methyl-acrylate*</u> **4h** : ***E* *isomer*** [15d]. IR (KBr) (cm^{-1}) : ν = 3140, 2970, 1690 (CO), 1628, 1472, 1360, 1260, 1110 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.49 (d, $^3J_{Ha,Hb}$ = 1.87 Hz, 1H, *H*$_a$), 7.42 (d, $^4J_{CH3,H}$ = 1.26 Hz, 1H, C*H*=C-CH$_3$), 6.56 (d, $^3J_{Hc,Hb}$ = 3.46 Hz, 1H, *H*$_c$), 6.44 (dd, $^3J_{Hb,Hc}$ = 3.46 Hz, $^3J_{Hb,Ha}$ = 1.87 Hz, 1H, *H*$_b$), 4.21 (q, $^3J_{H,H}$ = 7.12 Hz, 2H, CH$_3$C*H*$_2$O), 2.18 (d, $^4J_{CH3,H}$ = 1.38 Hz, 3H, CH=C-C*H*$_3$), 1.29 (t, $^3J_{H,H}$ = 7.12 Hz, 3H, *C*H$_3$CH$_2$O). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 168.35 (*C*O), 151.93 (*C*$_d$), 143.75 (*C*$_a$), 125.50 (*C*=C-CO), 124.98 (C=*C*-CO), 114.58-111.92 (*C*$_c$, *C*$_b$), 60.73 (*C*H$_2$CH$_3$), 14.22 (CH$_2$*C*H$_3$), 13.95 (C=C-*C*H$_3$). MS (EI) : *m / z* (%) 180 (M^+, 100), 152 (66), 135 (84), 106 (69). Anal. Calcd. for $C_{10}H_{12}O_3$: H, 6.72 ; C, 66.64 ; O, 26.65. Found : H, 6.93 ; C, 65.92 ; O, 26.31.

E* + *Z* *isomer (mixture). Identification of the *Z* isomer (by comparison with the spectra of the isolated *E* isomer). ^{1}H-NMR ($CDCl_3$) : δ = 7.34 (d, $^3J_{Ha,Hb}$ = 1.87 Hz, 1H, *H*$_a$), 6.85 (d, $^3J_{Hc,Hb}$ = 3.46 Hz, 1H, *H*$_c$) 6.45 (1H, C*H*=C-CH$_3$), 6.37 (dd, $^3J_{Hb,Hc}$ = 3.45 Hz, $^3J_{Hb,Ha}$ = 1.85 Hz, 1H, *H*$_b$), 4.10 (q, $^3J_{H,H}$ = 7.12 Hz, 2H, CH$_3$C*H*$_2$O), 2.05 (d, $^4J_{CH3,H}$ = 1.61 Hz, 3H, CH=C-C*H*$_3$), 1.20 (t, $^3J_{H,H}$ = 7.12 Hz, 3H, *C*H$_3$CH$_2$O). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 168.45 (*C*O), 150.72 (*C*$_d$), 142.50 (*C*$_a$), 123.16 (*C*=C-CO), 125.71 (C=*C*-CO), 112.26-111.71 (*C*$_c$, *C*$_b$), 60.50 (*C*H$_2$CH$_3$), 14.13 (CH$_2$*C*H$_3$), 21.38 (C=C-*C*H$_3$).

<u>*Ethyl 5-phenyl-2,4-pentadienoate*</u> **4i** : Ph-H$_d$C$_d$=C$_c$H$_c$-H$_b$C$_b$=C$_a$H$_a$-CO$_2$Et : ***EE* *isomer***. IR (KBr) (cm^{-1}) : ν = 2890, 1695 (CO), 1610, 1440, 1230, 1150, 1110, 985 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.50-7.30 (m, 5H, C$_6$*H*$_5$), 7.35 (m, 1H, *H*$_b$), 6.89 (d, $^3J_{Hd,Hc}$ = 15.40 Hz, 1H, *H*$_d$), 6.86 (dd, $^3J_{Hc,Hb}$ = 10.3 Hz, $^3J_{Hc,Hd}$ = 15.40 Hz, 1H, *H*$_c$), 6 (d, $^3J_{Ha,Hb}$ = 15.31 Hz, 1H, *H*$_a$), 4.23 (q, $^3J_{H,H}$ = 7.14 Hz, 2H, CH$_3$C*H*$_2$O), 1.31 (t, $^3J_{H,H}$ = 7.14 Hz, 3H, *C*H$_3$CH$_2$O). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 167.05 (*C*O), 144.5 (*C*$_b$), 140.35 (*C*$_c$), 136.06 (*i*-*C*, C$_6$H$_5$), 129.23, 128.80, 127.18 (*o*-*C*, *m*-*C*, *p*-*C*, C$_6$H$_5$), 126.26 (*C*$_d$), 121.35 (*C*$_a$), 60.34 (*C*H$_2$CH$_3$), 14.13 (CH$_2$*C*H$_3$). MS (EI) : *m / z* (%) 202 (M^+, 30), 157 (47), 129 (100). Anal. Calcd. for $C_{13}H_{14}O_2$: H, 6.98 ; C, 77.19 ; O, 15.83. Found : H, 7.15 ; C, 76.97 ; O, 15.44.

EZ* + *EE* *isomer.(mixture). Identification of the *EZ* isomer (by comparison with the spectra of the isolated *EE* isomer). ^{1}H-NMR ($CDCl_3$) : δ = 8.17 (ddd, $^4J_{Hc,Ha}$ = 1.02 Hz, $^3J_{Hc,Hb}$ = 11.40 Hz, $^3J_{Hc,Hd}$ = 15.70 Hz, 1H, *H*$_c$), 7.55-7.23 (m, 5H, C$_6$*H*$_5$), 6.82 (dd, $^3J_{Hd,Hc}$ = 15.70 Hz, $^4J_{Hd,Hb}$ = 1.05 Hz, 1H, *H*$_d$), 6.75 (dd, $^3J_{Hb,Hc}$ = 11.4 Hz, $^3J_{Hb,Ha}$ = 11.3 Hz, 1H, *H*$_b$), 5.73 (d, $^3J_{Ha,Hb}$ = 11.30 Hz, 1H, *H*$_a$), 4.23 (q, $^3J_{H,H}$ = 7.13 Hz, 2H, CH$_3$C*H*$_2$O), 1.30 (t, $^3J_{H,H}$ = 7.13 Hz, 3H, *C*H$_3$CH$_2$O).

Ethyl 2-methyl-5-phenyl-2,4-pentadienoate **4j** : Ph-H_dC_d=C_cH_c-H_bC_b=$C_a(CH_3)CO_2Et$

EE isomer. IR (KBr) (cm^{-1}) : ν = 3000, 2940, 2900, 1690 (CO), 1610, 1430, 1350, 1270, 1220, 1090, 960 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.50-7.29 (m, 6H, C_6H_5 and H_b), 7.08 (dd, $^3J_{Hc,Hd}$ = 15.33 Hz, $^3J_{Hc,Hb}$ = 11.05 Hz, 1H, H_c), 6.86 (d, $^3J_{Hd,Hc}$ = 15.33 Hz, 1H, H_d), 4.25 (q, $^3J_{H,H}$ = 7.15 Hz, 2H, CH_3CH_2O), 2.10 (d, $^4J_{CH_3,Hb}$ = 1.24 Hz, 3H, CH=C-CH_3), 1.34 (t, $^3J_{H,H}$ = 7.15 Hz, 3H, CH_3CH_2O). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 168.34 (CO), 138.95 (C_b), 138.20 (C_c), 136.65 (*i*-C, C_6H_5), 128.77, 128.67, 127.06 (*o*-C, *m*-C, *p*-C, C_6H_5), 127.51 (C_a), 123.97 (C_d), 60.59 (CH_2CH_3), 14.36 (CH_2CH_3), 12.89 (C=C-CH_3). MS (EI) : *m / z* (%) 216 (M^+, 45), 187 (10), 171 (22), 143 (100), 128 (82). Anal. Calcd. for $C_{14}H_{16}O_2$: H, 7.46 ; C, 77.74 ; O, 14.80. Found : H, 7.59 ; C, 77.61 ; O, 14.45.

EZ + EE isomer.(mixture). Identification of the *EZ* isomer (by comparison with the spectra of the isolated *EE* isomer) . ^{1}H-NMR ($CDCl_3$) : δ = 7.50-7.27 (m, 5H, C_6H_5), 7.95 (dd, $^3J_{Hc,Hd}$ = 15.62 Hz, $^3J_{Hc,Hb}$ = 11.30 Hz, 1H, H_c), 6.70 (d, $^3J_{Hd,Hc}$ = 15.60 Hz, 1H, H_d), 6.60 (dq, $^3J_{Hb,Hc}$ = 11.30 Hz, $^4J_{Hb,CH_3}$ = 1.20 Hz, 1H, H_b), 4.27 (q, $^3J_{H,H}$ = 7.15 Hz, 2H, CH_3CH_2O), 2.04 (d, $^4J_{CH_3,Hb}$ = 1.22 Hz, 3H, CH=C-CH_3), 1.38 (t, $^3J_{H,H}$ = 7.15 Hz, 3H, CH_3CH_2O).

Ethyl 5-phenyl-2-hexenoate **4k** : ***E isomer***. IR (KBr) (cm^{-1}) : ν = 2972, 1716 (CO), 1643, 1453, 1280, 1180, 815 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.35-7.15 (m, 5H, C_6H_5), 6.86 (m, 1H, C*H*=CH-CO), 5.80 (dt, $^3J_{H,H}$ = 15.8 Hz, $^4J_{H,CH_2}$ = 1.57 Hz, 1H, CH=C*H*-CO), 4.17 (q, $^3J_{H,H}$ = 7.13 Hz, 2H, CH_3CH_2O), 3.12-2.83 (m, 3H, C*H*-CH_2), 1.31 (d, $^3J_{H,H}$ = 6.4 Hz, 3H, CH-CH_3), 1.29 (t, $^3J_{H,H}$ = 7.13 Hz, 3H, CH_3CH_2O). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 166.45 (CO), 148.53 (C=C-CO), 146.31 (*i*-C, C_6H_5), 128.53, 127.05 (*o*-C, *m*-C, C_6H_5), 126.18 (*p*-C, C_6H_5), 120.51 (C=C-CO), 59.83 (CH_2CH_3), 39.88 (CH-CH_3), 37.0 (CH_2-C=C), 22 (CH-CH_3), 14.29 (CH_2CH_3). MS (EI) : *m / z* (%) 218 (M^+, 15), 132 (26), 105 (100). Anal. Calcd. for $C_{14}H_{18}O_2$: H, 8.32 ; C, 77.02 ; O, 14.67. Found : H, 8.65 ; C, 76.75 ; O, 15.42.

Ethyl 2-methyl-5-phenyl-2-hexenoate **4l** : ***E isomer***. IR (KBr) (cm^{-1}) : ν = 3075, 3050, 2920, 1700 (CO), 1640, 1495, 1450, 1410, 1260 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.36-7.16 (m, 5H, C_6H_5), 6.77 (qt, $^4J_{H,CH_3}$ = 1.45 Hz, $^3J_{H,H}$ = 7.55 Hz, 1H, C*H*=C-CO), 4.20 (q, $^3J_{H,H}$ = 7.11 Hz, 2H, CH_3CH_2O), 2.96-2.88 (m, 1H, C*H*CH_2), 2.50-2.42 (m, 2H, CHCH_2), 1.80 (d, $^4J_{CH_3,H}$ = 1.45 Hz, 3H, CH=C-CH_3), 1.35-1.25 (m, 6H, CH_3CH_2O and CH_3CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 168.11 (CO), 146.47 (*i*-C, C_6H_5), 140.30 (C=C-CO), 128.76 (C=C-CO), 128.45, 126.85 (*o*-C, *m*-C, C_6H_5), 126.24 (*p*-C, C_6H_5), 60.39 (CH_2CH_3), 39.45 (CH-CH_3), 37.46 (CH_2-C=C), 21.53 (CH-CH_3), 14.28 (CH_2CH_3), 12.47 (C=C-CH_3). MS (EI) : *m / z* (%) 232 (M^+, 12), 105 (100), 128 (36). Anal. Calcd. for $C_{15}H_{20}O_2$: H, 8.68 ; C, 77.54 ; O, 13.78. Found : H, 9.19 ; C, 76.18 ; O, 14.10.

E + Z isomer (mixture). ^{1}H-NMR ($CDCl_3$) : identification of the Z isomer (by comparison with the spectra of the isolated *E* isomer) : δ = 7.34-7.15 (m, 5H, C_6H_5), 5.85 (qt, $^4J_{H,CH_3}$ = 1.40 Hz, $^3J_{H,H}$ = 6.80 Hz, 1H, C*H*=C-CH_3), 4.18 (q, $^3J_{H,H}$ = 7.11 Hz, 2H, CH_3CH_2O), 2.96-2.71 (m, 3H, C*H*-CH_2), 1.87 (d, $^4J_{CH_3,H}$ = 1.40 Hz, 3H, CH=C-CH_3), 1.30-1.22 (m, 6H, CH_3CH_2O and CH_3CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 168.04 (CO), 146.74 (*i*-C, C_6H_5), 141.04 (C=C-CO), 128.37 (C=C-CO), 128.07, 128.04 (*o*-C, *m*-C, C_6H_5), 126.05 (*p*-C, C_6H_5), 60.05 (CH_2CH_3), 40.14 (CH-CH_3), 37.71 (CH_2-C=C), 22.02 (CH-CH_3), 20.06 (C=C-CH_3), 14.28 (CH_2CH_3).

Ethyl (4-phenylcyclohexylidene)-acetate **4m** : IR (KBr) (cm^{-1}) : ν = 2095, 1710 (CO), 1600, 1420, 1240 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.35-7.18 (m, 5H, C_6H_5), 5.70 (m, 1H, C=C*H*-CO), 4.21 (q, $^3J_{H,H}$ = 7.14 Hz, 2H, CH_3CH_2O), 2.90-2.80 (m, 1H, Ph-C*H*), 2.50-1.70 (m, 8H, $C_6H_1H_8$), 1.30 (t, $^3J_{H,H}$ = 7.14 Hz, 3H, CH_3CH_2O). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 171.9 (*C*O), 146.8 (*i-C*, C_6H_5), 131.2 (*C*=C-CO), 128.40, 126.90, 126.06 (*o-C*, *m-C*, *p-C*, C_6H_5), 125.30 (C=*C*-CO), 60.34 (CH_2CH_3), 43.26, 33.54, 29.87, 29.08 (4 CH_2, C_6H_9), 39.71 (Ph-*C*H), 14.36 (CH_2CH_3). MS (EI) : *m / z* (%) 244 (M^+, 61), 199 (20), 171 (20), 140 (76), 112 (100). Anal. Calcd. for $C_{16}H_{20}O_2$: H, 8.26 ; C, 78.64 ; O, 13.10. Found : H, 8.45 ; C, 78.57 ; O, 12.84.

Ethyl 2-(4-phenylcyclohexylidene)-propionate **4n** : IR (KBr) (cm^{-1}) : ν = 3010, 1695 (CO), 1605, 1430, 1255 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 7.35-7.16 (m, 5H, C_6H_5), 4.23 (q, $^3J_{H,H}$ = 7.14 Hz, 2H, CH_3CH_2O), 3.23-3.15 (m, 1H, Ph-C*H*), 2.83-2.70 (m, 2H, $C_6H_7H_2$), 2.22-1.97 (m, 4H, $C_6H_5H_4$), 1.93 (s, 3H, C=C-CH_3), 1.75-1.51 (m, 2H, $C_6H_7H_2$), 1.33 (t, $^3J_{H,H}$ = 7.17 Hz, 3H, CH_3CH_2O). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 170.56 (*C*O), 146.4 (*i-C*, C_6H_5), 145.90 (C=*C*-CO), 128.40, 126.84, 126.12 (*o-C*, *m-C*, *p-C*, C_6H_5), 120.6 (*C*=C-CO), 60.23 (CH_2CH_3), 44.4 (Ph-*C*H), 35.24, 34.87, 32.03, 30.90 (4 CH_2, C_6H_9), 15.29 (C=C-CH_3), 14.31 (CH_2CH_3). MS (EI) : *m / z* (%) 258 (M^+, 100), 213 (54), 184 (20), 154 (58), 126 (65), 104 (54), 91 (90). Anal. Calcd. for $C_{17}H_{22}O_2$: H, 8.59 ; C, 79.02 ; O, 12.39. Found : H, 8.81 ; C, 79.15 ; O, 12.56.

trans-stilbene **6o** : mp : 124°C. ^{1}H-NMR ($CDCl_3$) : δ = 7.55-7.05 (m, 12H).

trans-p-Nitrostilbene **6p** : mp : 158°C. ^{1}H-NMR ($CDCl_3$) : δ = 8.25-8.16 (m, 2H), 7.65-7.05 (m, 9H) .

General procedure for the synthesis of α,β-unsaturated acids (5).

Under nitrogen atmosphere, the phosphonium salt [16] (10 mmol) corresponding to the diylide **2a** (R = H) or **2b** (R = Me or Et) is introduced in anhydrous THF (100 ml). To the heterogeneous mixture, cooled at -50 °C, a solution of *n*-butyllithium 2.5 N in hexane (8 ml, 20 mmol) is added dropwise. After 30 mn at this temperature, the solution is allowed to warm up to room temperature. Then, 10 mmol of ethyl carbonate are added to the reaction mixture and after 15 minutes at room temperature, the carbonyl compound (20 mmol) is then added quickly.

The THF is evaporated after 10 minutes at 20°C, in the case of **2a** or **2b** and enolisable or non enolisable aldehydes. For **2a** and phenylcyclohexanone the evaporation of the solvent is performed after two days in refluxing THF.

Then in all the cases, the residue is hydrolysed by a NaOH solution (1N : 50ml), during 2 or 3 hours at room temperature. After extraction with CH_2Cl_2 (3 x 50ml), the aqueous layer is acidified until the formation of a precipitate. After filtration this last one is recristalized in EtOH/H_2O to give the corresponding α,β-unsaturated acids **5** (***E*** isomer).

Cinnamic acid **5e** : mp : 132°C. IR (KBr) (cm^{-1}) : ν = 3447, 3060, 1680 (CO), 1626, 1445, 1280, 977 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 8.61 (bs, 1H, CO_2H), 7.83 (d, $^3J_{H,H}$ = 16 Hz, 1H, C*H*=CH-CO), 7.58-7.42 (m, 5H, C_6H_5), 6.55 (d, $^3J_{H,H}$ = 16 Hz, 1H, CH=C*H*-CO). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 173.50 (*C*O), 148.2 (*C*=C-

CO), 135.9 (*i-C*, C_6H_5), 129.50, 128.43, 128.40 (*o-C*, *m-C*, *p-C*, C_6H_5), 118.75 (C=C-CO). Anal. Calcd. for $C_9H_8O_2$: H, 5.45 ; C, 72.95 ; O, 21.61. Found : H, 5.55 ; C, 72.99 ; O, 21.85.

2-methylcinnamic acid **5f** [15e] : mp : 79°C. IR (KBr) (cm^{-1}) : ν = 3425, 3040, 1662 (CO), 1609, 1443, 1407, 1260, 680 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 11 (bs, 1H, CO_2H), 7.84 (q, $^4J_{H,CH_3}$ = 1.20 Hz, 1H, C*H*=C-CH_3) 7.45-7.34 (m, 5H, C_6H_5), 2.12 (d, $^4J_{CH_3,H}$ = 1.20 Hz, 1H, CH=C-C*H*$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 174.36 (*C*O), 141.11 (*C*=C-CO), 135.63 (*i-C*, C_6H_5), 129.85 (*m-C*, C_6H_5), 128.71 (*o-C*, C_6H_5), 128.70 (*p-C*, C_6H_5), 127.64 (C=*C*-CO), 13.73 (C=C-*C*H_3). MS (EI) : *m / z* (%) 162 (M^+, 100), 116 (90), 91 (57), 51 (36). Anal. Calcd. for $C_{10}H_{10}O_2$: H, 6.22 ; C, 74.04 ; O, 19.74. Found : H, 6.27 ; C, 73.98 ; O, 19.85.

2-ethylcinnamic acid **5r** [15f] : mp : 105°C. IR (KBr) (cm^{-1}) : ν = 3425, 3057, 2960, 1682 (CO), 1618, 1420, 1310, 1260, 940 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 13.24 (bs, 1H, CO_2H), 7.83 (s, 1H, C*H*=C-CH_2), 7.45-7.36 (m, 5H, C_6H_5), 2.61 (q, $^3J_{H,H}$ = 7.40 Hz, 2H, -C*H*$_2$CH$_3$), 1.25 (t, $^3J_{H,H}$ = 7.40 Hz, 3H, CH_2C*H*$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 173.95 (*C*O), 140.78 (*C*=C-CO), 135.51 (*i-C*, C_6H_5), 134 (C=*C*-CO), 129.38, 128.70, 128.54 (*o-C*, *m-C*, *p-C*, C_6H_5), 20.57 (*C*H_2CH$_3$), 13.75 (CH_2*C*H_3). MS (EI) : *m / z* (%) 176 (M^+, 100), 130 (85), 91 (54). Anal. Calcd. for $C_{11}H_{12}O_2$: H, 6.87 ; C, 74.96 ; O, 18.17. Found : H, 6.59 ; C, 75.16 ; O, 18.39.

p-nitrocinnamic acid **5s** [15g] : mp : 286°C. IR (KBr) (cm^{-1}) : ν = 3415, 1685 (CO), 1625, 1517, 1421, 1338, 1302, 1280, 985 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 12.74 (bs, 1H, CO_2H), 8.23-7.93 (m, 5H, C_6H_5), 7.68 (d, $^3J_{H,H}$ = 16.10 Hz, 1H, C*H*=CH-CO), 6.72 (d, $^3J_{H,H}$ = 16.10 Hz, 1H, CH=C*H*-CO. ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 166.92 (*C*O), 147.84 (*p-C*, C_6H_5), 141.20 (Ph-*C*H), 140.65 (*i-C*, C_6H_5), 129.17 (*o-C*, C_6H_5), 123.8 (*m-C*, C_6H_5), 123.53 (=*C*-CO). MS (EI) : *m / z* (%) 193 (M^+, 100), 176 (43), 147 (29), 91 (58). Anal. Calcd. for $C_9H_7NO_4$: H, 3.65 ; C, 55.95 ; O, 33.14 ; N, 7.25. Found : H, 3.62 ; C, 56.09 ; O, 33.35 ; N, 7.32.

3-(2-furyl)-acrylic acid **5g** [15h] : mp : 141°C. IR (KBr) (cm^{-1}) : ν = 3405, 2990, 1710 (CO), 1585, 1445, 1320, 1240, 905 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 10 (bs, 1H, CO_2H), 7.52 (d, $^3J_{H,H}$ = 15.72 Hz, 1H, C*H*=CH-CO), 7.50 (d, $^3J_{Ha,Hb}$ = 1.49 Hz, 1H, *H*$_a$), 6.68 (d, $^3J_{Hc,Hb}$ = 3.37 Hz, 1H, *H*$_c$), 6.49 (dd, $^3J_{Hb,Hc}$ = 3.40 Hz, $^3J_{Hb,Ha}$ = 1.50 Hz, 1H, *H*$_b$), 6.30 (d, $^3J_{H,H}$ =15.72 Hz, 1H, CH=C*H*-CO). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 172.62 (*C*O), 150.65 (*C*$_d$), 145.32 (*C*$_a$), 133.07 (*C*=C-CO) 114.88 (C=*C*-CO), 115.83-112.48 (*C*$_c$, *C*$_b$). MS (EI) : *m / z* (%) 138 (M^+, 100), 121 (43), 110 (31), 92 (27). Anal. Calcd. for $C_7H_6O_3$: H, 4.38 ; C, 60.86 ; O, 34.76. Found : H, 4.35 ; C, 60.84 ; O, 34.80.

5-phenylpenta-2,4-dienoic acid **5i** [15i] Ph-C*H*$_d$=C*H*$_c$-C*H*$_b$=C*H*$_a$-CO_2H

***EE** isomer.* mp : 163°C (165 Lit). IR (KBr) (cm^{-1}) : ν = 3420, 3045, 1685 (CO), 1620, 1295, 990 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 12.28 (bs, 1H, CO_2H), 7.60-6.95 (m, 8H, C_6H_5, *H*$_b$, *H*$_c$ and *H*$_d$), 6.0 (d, $^3J_{Ha,Hb}$ = 15.30 Hz, 1H, *H*$_a$). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 167.46 (*C*O), 144.22 (C_b), 139.72 (C_c), 135.90 (*i-C*, C_6H_5), 128.85, 128.75, 127.06 (*o-C*, *m-C*, *p-C*, C_6H_5), 126.53 (C_d), 122.19 (C_a). MS (EI) : *m / z* (%) 174 (M^+, 8), 157 (22), 129 (100), 115 (8), 102 (11). Anal. Calcd. for $C_{11}H_{10}O_2$: H, 5.79 ; C, 75.83 ; O, 18.38. Found : H, 5.95 ; C, 75.76.

5-phenyl-2-pentenoic acid **5t** : mp : 104°C. IR (KBr) (cm^{-1}) :ν = 3405, 3070, 1690 (CO), 1590, 1405, 1295, 1272, 1230, 987 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 11.15 (bs, 1H, CO_2H), 7.37-7.08 (m, 6H, C_6H_5 and C*H*=CH-CO), 5.88 (d, $^3J_{H,H}$ = 15.70 Hz, 1H, CH=C*H*-CO), 2.83 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, Ph-C*H*$_2$), 2.64-2.04 (m, 2H,

Ph-CH_2-CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 172.16 (*C*O), 151.08 (*C*=C-CO), 140.60 (*i-C*, C_6H_5), 128.55, 128.35, 126.28 (*o-C*, *m-C*, *p-C*, C_6H_5), 121.19 (C=*C*-CO), 34.19, 34 (2 *C*H_2). MS (EI) : *m / z* (%) 176 (M^+, 5), 213 (54), 130 (15), 91 (100). Anal. Calcd. for $C_{11}H_{12}O_2$: H, 6.87 ; C, 74.96 ; O, 18.17. Found : H, 6.95 ; C, 75.04 ; O, 17.95.

(4-phenylcyclohexylidene)-acetic acid **5m** : mp : 119°C. IR (KBr) (cm^{-1}) : ν = 3400, 3005, 1700 (CO), 1597, 1487, 1405, 1392, 1328, 1225, 915 cm^{-1}. ^1H-NMR ($CDCl_3$) : δ = 10.89 (bs, 1H, CO_2H) 7.36-7.18 (m, 5H, C_6H_5), 5.74 (m, 1H, C=C*H*), 3.09-2.78 (m, 1H, Ph-C*H*), 2.41-2.15 (m, 4H, H_2C-CH-CH_2), 2.14-1.74 (m, (H_2C)$_2$C=C). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 178.45 (*C*O), 147.1 (*i-C*, C_6H_5), 130.82 (*C*=C-CO), 128.42, 126.86, 126.12 (*o-C*, *m-C*, *p-C*, C_6H_5), 126.10 (C=*C*-CO), 42.92, 33.54, 29.84, 29.08 (4 *C*H_2, C_6H_9), 39.65 (Ph-*C*H). MS (EI) : *m / z* (%) 216 (M^+, 45), 171 (25), 104 (100). Anal. Calcd. for $C_{14}H_{16}O_2$: H, 7.46 ; C, 77.74 ; O, 14.80. Found : H, 7.48 ; C, 77.72 ; O, 14.91.

1,4-phenylenediacrylic acid **5u** : *Mixture of isomers* : MS (EI) : *m / z* (%) 218 (M^+, 100), 173 (38), 127 (29). Anal. Calcd. for $C_{12}H_{10}O_4$: H, 4.62 ; C, 66.04 ; O, 29.34. Found : H, 4.35 ; C, 65.97 ; O, 29.68.

***Procedure for the synthesis of the methyldiphenyl(carbethoxymethyl)phosphonium iodide (3"a)*.**

Under nitrogen atmosphere, the dimethyldiphenylphosphonium iodide [16] (5 mmol) corresponding to the diylide **2a** (R = H) is introduced in anhydrous THF (50 ml). To the heterogeneous mixture, cooled at -50 °C, a solution of *n*-butyllithium 2.5 N in hexane (4 ml, 10 mmol) is added dropwise. After 30 mn, the solution is allowed to warm up to room temperature and 5 mmol of ethyl carbonate are added to the reaction mixture.

After 15 mn the solution is hydrolysed with HCl (100 ml, 0.2 N) and the THF is evaporated under reduce pressure. Then the remaining aqueous layer is extracted with CH_2Cl_2 (3 X 100 ml) and the organic layer is dried over Na_2SO_4. After filtration and concentration, an oil is obtained which gives after recristallization ($CHCl_3$ / Et_2O) the corresponding phosphonium salt **3a"** (yield : 92%).

mp : 136-138°C. ^{31}P-NMR ($CDCl_3$) : δ = 21.10 ppm. ^1H-NMR ($CDCl_3$) : δ = 7.98-7.65 (m, 10H, 2 C_6H_5), 4.91 (d, $^2J_{P,H}$ = 13.6 Hz, 2H, P-C*H*$_2$), 4.06 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.0 (d, $^2J_{P,H}$ = 14.1 Hz, 3H, P-C*H*$_3$), 1.08 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, OCH$_2$C*H*$_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 164.2 (d, $^2J_{C,P}$ = 3.9 Hz, *C*O$_2$Et), 135.1 (d, $^4J_{C,P}$ = 3.1 Hz, *p-C* of C_6H_5), 132.8 (d, $^2J_{C,P}$ = 10.64 Hz, *o-C* of C_6H_5), 130.2 (d, $^3J_{C,P}$ = 13 Hz, *m-C* of C_6H_5), 118.4 (d, $^1J_{C,P}$ = 88 Hz, *i-C* of C_6H_5), 62.9 (s, OCH$_2$CH$_3$), 32.3 (d, $^1J_{C,P}$ = 57.5 Hz, P-*C*H$_2$-CO), 13.9 (s, OCH$_2$*C*H$_3$), 10.0 (d, $^1J_{C,P}$ = 56.2 Hz, P-*C*H$_3$). Anal. Calcd. for $C_{16}H_{18}O_2P$: H, 4.83 ; C, 49.27 ; O, 7.73. Found : H, 4.87 ; C, 49.45 ; O, 8.03.

***Procedure for the synthesis of the benzyldiphenyl(carbethoxybenzyl)phosphonium bromide (3"c)*.**

Under nitrogen atmosphere, the dibenzyldiphenylphosphonium iodide [16] (5 mmol) corresponding to the diylide **2c** (R = Ph), is introduced in anhydrous THF (50 ml). To the heterogeneous mixture, cooled at -50 °C, a solution of *n*-butyllithium 2.5 N in hexane (4 ml, 10 mmol) is added dropwise. After 30 mn, the solution is allowed to warm up to room temperature and 5 mmol of ethyl carbonate are added to the reaction mixture.

After 15 mn the solution is hydrolysed with CF_3CO_2H (10 mmol) and a precipitate appears immediately. After filtration the organic layer is washed with water (2 X 100 ml) and dried over $MgSO_4$. The precipitate corresponds to the starting dimethyldiphenylphosphonium bromide[16] (yield 40%). The organic phase is concentrated to give an oil which gives after recristallization ($CHCl_3$ / Et_2O) the corresponding phosphonium salt **3"e** (yield : 52%).

mp : 132-134°C. ^{31}P-NMR ($CDCl_3$) : δ = 28.90 ppm. ^{1}H-NMR ($CDCl_3$) : δ = 7.73-6.67 (m, 21H, P-C*H* and 4 C_6H_5), 4.23-4.09 (m, 4H, P-CH_2 and OCH_2CH$_3$), 1.13 (t, $^3J_{H,H}$ = 7.10 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 167.6 (s, CO_2Et), 135.64-127.87 (m, *o-C*, *m-C*, *p-C* of 4 C_6H_5), 127.49 and 127.35 (two doublets, $^2J_{C,P}$ = 3.76 Hz and $^2J_{C,P}$ = 5.53 Hz, *ipso* aromatic carbons of C_6H_5-CH_2 and of C_6H_5-CH), 115.30 and 113.64 (two doublets, $^1J_{C,P}$ = 74.24 Hz and $^1J_{C,P}$ = 74.44 Hz, *ipso* aromatic carbons of C_6H_5-P), 62.94 (s, OCH_2CH_3), 48.19 (d, $^1J_{C,P}$ = 49.09 Hz, P-CH), 28.60 (d, $^1J_{C,P}$ = 46.45 Hz, P-CH_2), 13.61 (s, OCH_2CH_3). FAB$^+$ (NBA) m/z = 439 (M^+ 100%), 366 (6%) 275 (8%) 185 (12%).

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