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

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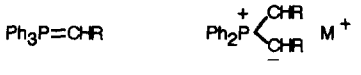
Abstract : The reactivity of diphenylphosphonium diylides was investigated towards carbonic anhydride derivatives. Unsubstituted and substituted non-stabilized diylides react with phenylisocyanate and dicyclohexylcarbodiimide, leading to the formation of new monoylide type intermediates. These last ones react *in situ* with carbonyl compounds through a Wittig reaction leading respectively to α,β-unsaturated amides and amidines. Substituted semi-stabilized or stabilized diylides, in similar conditions lead to the formation of alkenes. In all the cases a high *E* stereoselectivity, determined by ^{1}H-NMR and ^{13}C-NMR, was observed .

Introduction

Phosphonium ylides **1** show a moderate nucleophilicity owing to the presence of a phosphorus bearing a positive charge (fig 1). Their application field in the Wittig reaction is then generally limited to the electrophilic carbonyl group of aldehydes and ketones .



1 **2**

Fig 1

Phosphonium diylides **2** have a stronger nucleophilicity than the corresponding monoylides, because the phosphorus empty orbitals involved in the "ylidic bond" are less able to stabilize simultaneously both carbanionic centers. Thanks to their higher nucleophilicity, the phosphonium diylides potentially have a wider application field than monoylides, especially regarding the Wittig reaction. Indeed, we have shown in previous works that the parent structure for diylides, the lithium dimethyldiphenylphosphonium diylide **2a**, non-stabilized and unsubstituted, is a very efficient tool in organic synthesis (fig 2).[1]

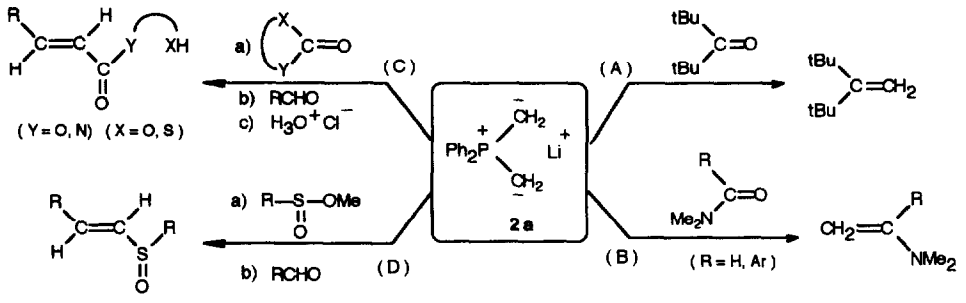


Fig 2

The direct carbonyl olefination of sterically hindered ketones [2] (path A), and non enolizable amides [3] (path B) respectively gives alkenes and enamines. On the other side, the diylide **2a** can react with carbamates, carbonates or sulfinates to provide new functionalized ylides which can be involved in a subsequent Wittig reaction yielding respectively α,β-unsaturated esters or amides [4] (path C) or α,β-unsaturated sulfoxides (with possibility of enantioselective synthesis) [5] (path D).

The amount and the diversity of the results obtained with the diylide **2a** led us to decide to extend our studies to substituted diylides (non-stabilized **2b**, semi-stabilized **2c** or stabilized **2d**) in order to settle the limitations of reactivity for these compounds in organic synthesis (fig 3). Thus we already report that substituted diylides present a greater nucleophilicity than the corresponding monoylides **1** in Wittig type reactions towards carbonyl compounds, specially towards overcrowded ketones. [2]

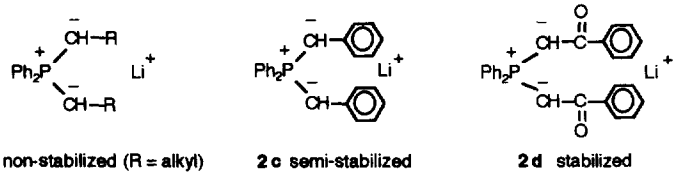


Fig 3

We report here the study on the reactivity of diylides **2a-2d** towards derivatives of carbonic anhydride such as phenylisocyanate and dicyclohexylcarbodiimide.

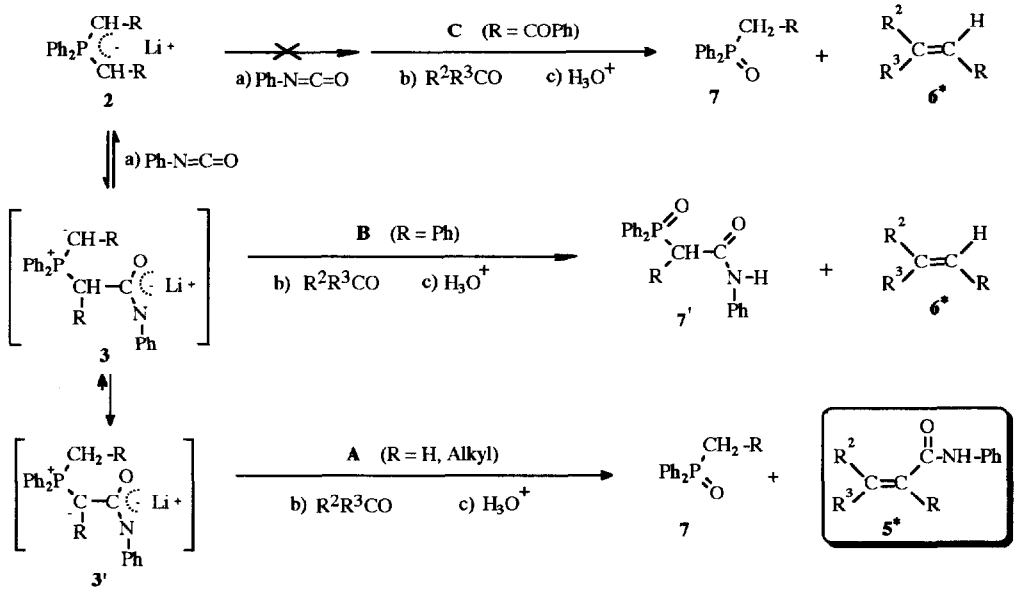
Recently, we have shown that this reaction, when performed with the unsubstituted non-stabilized diylide **2a**, enables the synthesis of α,β-unsaturated amides or amidines [6], giving one more example of the higher reactivity of diylides in comparison with the monoylides.

This reaction is also a good example to undertake a general study of the reactivity of the three kinds of diylides and to determine the scope and limitation of their applications.

Results and discussion

The non-stabilized diylides **2a** and **2b** (R = H, Me, *n*-Pr) can react equimolecularly with phenylisocyanate to give the corresponding intermediate phosphonium monoylides **3** (fig 4). The latter, through an intramolecular proton transfer, are transformed into new monoylides **3'** which get a weak semi-stabilized character due to the anionic metalated function in the α position.

The monoylides **3'** are less reactive than the monoylides **3** but they can react with non-enolizable aldehydes such as benzaldehyde, tolualdehyde or cinnamaldehyde to afford differently substituted α,β-unsaturated amides **5** (table 1 : entries 1, 2, 3, 4 ; fig 4 : path A). The good yield obtained with the parent structure (R = H) slightly decreases with the substituted diylides (R = Me, *n*-Pr), indicating that steric factors also must taken into account in that kind of reaction. The reaction can be generalized to enolizable aldehydes. Therefore, with the methyl substituted diylide **2b**, the phenylisocyanate and 3-phenylpropanal can react to give a good yield of the corresponding α,β-unsaturated amide (table 1 ; entry 5).



2a : R = H ; **2b** : R = Alkyl ; **2c** : R = Ph ; **2d** : R = COPh .
(* For the actual *E/Z* stereochemistry see table 1)

Fig 4

With ketones, either enolizable or not, the unsubstituted diylide **2a** leads to moderate yields for the formation of the expected amides (table 1 : entries 6 and 7). Nevertheless, the use of a substituted diylide **2b**

(R = Me) almost blocks the reaction in the case of benzophenone and, in the case of 4-phenylcyclohexanone, essentially leads to the formation of 2-(4-phenylcyclohexylidene)-4-phenylcyclohexanone **4**, which is the auto-condensation product resulting from an aldol condensation followed by dehydration (table 1 : entries 8 and 9).

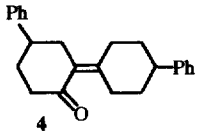


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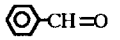
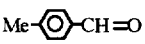
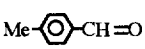
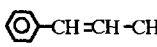
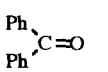
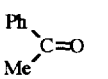
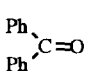
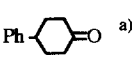
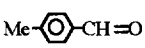
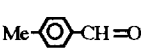
Table 1 : Synthesis of α,β-Unsaturated Amides **5** or Alkenes **6** by Reaction of the Diylides **2a** (R = H), **2b** (R = alkyl), **2c** (R = benzyl), **2d** (R = benzoyl) with Phenylisocyanate (Ph-N=C=O), Followed by Addition of Aldehydes or Ketones.

Entry	Diylides **2** R	$R^2R^3C{=}O$	Alkenes **6** Yields (%) [b]	(E / Z)	Amides **5**	Yields (%) [c]	(E / Z)
1	H		–		**5a**	77	100 / 0
2	Me		–		**5b**	60	94 / 6
3	*n*-Pr		–		**5c**	55	92 / 8
4	H		–		**5d**	75	100 / 0
5	Me	$PhCH_2CH_2$-CH=O	–		**5e**	67	76 / 24
6	H		–		**5f**	51	–
7	H		–		**5g**	40	84 / 16
8	Me		5	–	**5h**	10	–
9	Me	 [a]	–		**5i**	<5	–
10			68	100 / 0		–	
11	Ph		70	98 / 2	**5k**	<5	

a) Formation of the auto-condensation product **4** (identified by GCMS). b) Alkenes isolated by column chromatography.

c) Products isolated by column chromatography except for **5i** and **5k**, detected by GCMS.

Thus in the case of ketones, the steric hindrance of the carbanionic part in the diylides seems to play a major role and the formation of amides occurs mainly with the non-substituted diylide **2a** (R = H).

Using the stabilized diylide **2d** (R = CO-Ph), phenylisocyanate and tolualdehyde, the only olefination product formed is the alkene **6** (table 1, entry 10). This alkene may result from a Wittig reaction with the intermediate monoylide **3d** (fig 4 : path B) or from a direct Wittig reaction with the starting diylide **2d** (fig 4 : path C). The lattest hypothesis seems more likely for three reasons : (i) before tolualdehyde addition the only peak which can be observed *in situ* by ^{31}P-NMR corresponds to the stabilized starting diylide **2d** indicating a lack of reactivity of this compound towards the phenylisocyanate ; (ii) once the tolualdehyde added, the phosphine oxide **7d** is the only product to be observed *in situ* together with the alkene **6**. The formation of the phosphine oxide **7'd** (R = COPh) which could result from a Wittig reaction with the monoylide intermediate **3d**, is never observed ; (iii) protonation of the reaction mixture before tolualdehyde addition leads to the diphenacylphosphonium salt precursor of **2d** (fig 5, R = COPh), instead of the substituted phosphonium salt **3"d** corresponding to the intermediate formation of the monoylides **3d** and/or **3'd**.

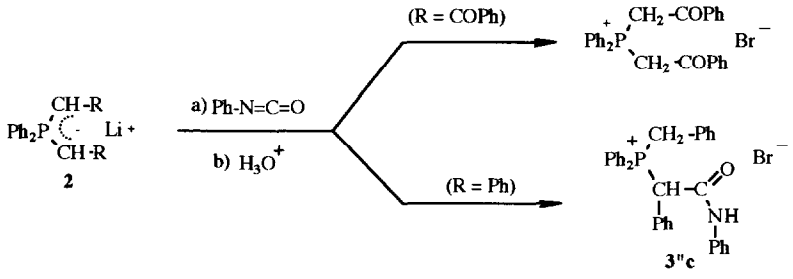


Fig 5

With the semi-stabilized diylide **2c** (R = Ph) phenylisocyanate and tolualdehyde, the olefination product obtained was also the alkene **6** (table 1, entry 11). However, in contrast with the diylide **2d**, after addition of phenylisocyanate, the full disappearance of the starting diylide **2c** was observed by ^{31}P-NMR, with simultaneous formation of six new signals, corresponding likely to the formation of several geometrical isomers of compounds **3c** and **3'c**. In accordance with these hypotheses, it was also possible to isolate the phosphonium salt **3"c** (yield : 60%), after acidic quenching of the reaction mixture before tolualdehyde addition (fig 5, R = Ph).

Therefore, in this case the starting diylide **2c** is probably not involved in the formation of the Wittig product **6**, the active species being then the intermediate monoylide **3c**. This hypothesis is corroborated by the fact that if the possibly unstable phosphine oxyde **7'c** has not been observed, neither has the phosphine oxide **7c** been, unlike the stabilized diylide **2d** case.

So, the semi-stabilized diylide **2c** (R = Ph) is a borderline case between the non-stabilized diylide **2b** for which the monoylide **3'b** is involved in the Wittig reaction, and the stabilized diylide **2d** which is directly involved as the Wittig reagent. To explain this middle character, it can be put forward that the presence of a

first semi-stabilizing group (R = Ph) does not prevent the reaction with phenylisocyanate leading then to the monoylide intermediate **3'c**.

But on this last one the conjugated effects on the same carbanionic position of the two semi-stabilizing groups (Ph and $PhNCO^-$) are too strong to enable the Wittig reaction unlike the case when R is an alkyl group. The reverse equilibrium between **3'c** and **3c** allows then a Wittig reaction starting from the minor species **3c** for which only one semi-stabilizating group is present on the active carbanionic position (fig 4 : path B).

A similar study has been realized using another derivative of carbonic anhydride, the dicyclohexylcarbodiimide (DCC) (fig 6).

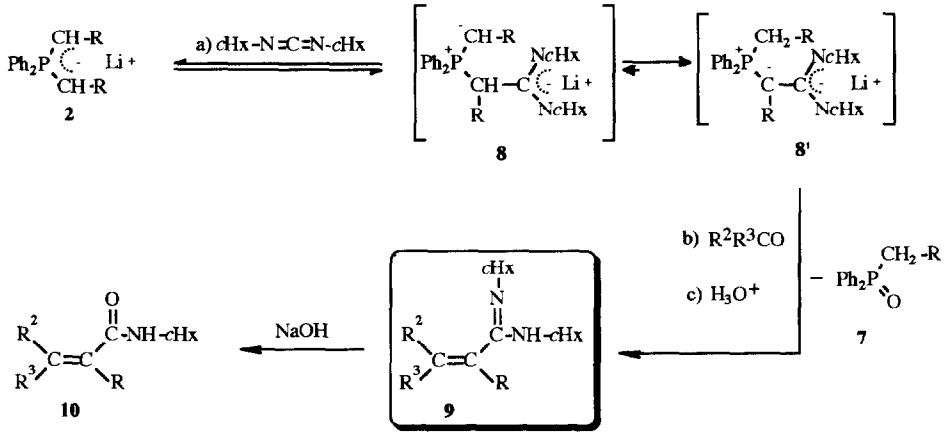


Fig 6

Thus, the non-stabilized diylides **2a** and **2b**, react with DCC to give the intermediate monoylides **8** then **8'**. The latter undergoes a Wittig reaction *in situ* with aldehydes to afford good yields of amidines **9** (fig. 6) which are not isolated, but hydrolyzed in alkaline conditions into amides **10** on account of an easier purification (table 2 : entries 12 and 13).

But, in the case of a non enolizable ketone, the reaction gives the direct Wittig olefination product **6** beside a very poor formation of amidines (table 2 : entry 14). And, in the same way as for phenylisocyanate, the reaction of the methyl substituted diylide with DCC then with enolizable ketones essentially leads to the formation of the auto-condensation product **4** (table 2 : entry 15).

The stabilized diylide **2d** leads, in the presence of tolualdehyde, to the formation of the Wittig reaction product **6** in a good yield (table 2 : entry 16). On the basis of the conclusions drawn from the former study with phenylisocyanate, it can be assumed that the ylide species involved in the reaction is likely the starting diylide **2d** (fig 7 : R = COPh)(**2d** does not react with DCC : the protonation of the reaction mixture before

addition of the tolualdehyde leads to the starting diphenacylphosphonium salt, and the only phosphine oxide formed in the Wittig reaction is the corresponding monophenacylphosphine oxide **7d**).

The semi-stabilized diylide **2c** leads, in the presence of DCC and tolualdehyde, to the formation of alkene **6** (table 2 : entry 17), likely involving, in the same way as with phenylisocyanate, the semi-stabilized intermediate **8** as the Wittig reagent (fig 7 : R = Ph).

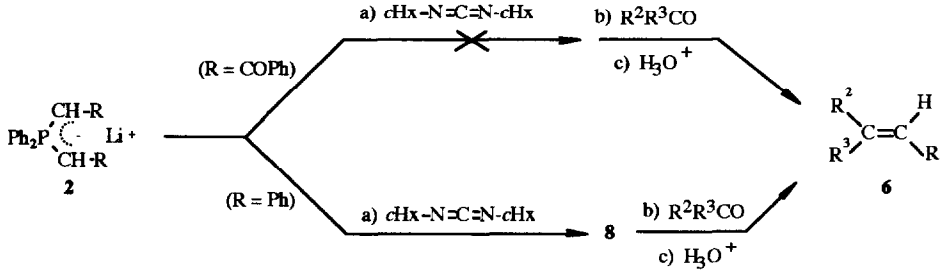
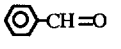
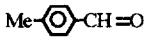
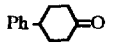


Fig 7 : **2c** : R = Ph ; **2d** : R = COPh .

Table 2 : Formation of α,β-Unsaturated N,N'-Disubstituted Amidines **9**, of the Corresponding Amides **10**, or Alkenes **6** by Reaction of the Diylides **2a-d** with Dicyclohexylcarbodiimide (DCC), Followed by Addition of Aldehydes or Ketones, and Subsequent Hydrolysis.

Entry	Diylides **2** R	$R^2R^3C=O$	Alkenes **6** Yields (%)[b]	(E / Z)	Amidines **9** Yields (%)[c]	(E / Z)
12	H		–		**9l** 80	100 / 0
13	Me		–		**9m** 60	95 / 5
14	Me		40		**9o** <5	
15	Me [a]		–		–	
16			68	98 / 2	–	
17	Ph		70	93 / 7	–	

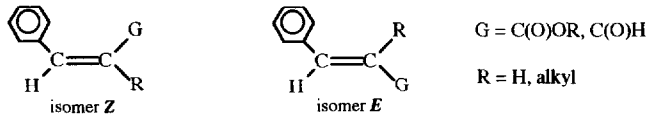
a) Formation of the auto-condensation product **4** (identified by GCMS). b) Alkenes isolated by column chromatography. c) Isolated yield of amides **10** after the basic hydrolysis of the amidines **9**.

In both cases, with phenylisocyanate or dicyclohexylcarbodiimide, we can observe a high *E* stereoselectivity in α,β–unsaturated amides.

When the unsubstituted diylide **2a** (R = H) is allowed to react with aldehydes (table 1 : entries 1, 4 ; table 2 : entry 12), the stereochemical assignement has been realized on the basis of ^{1}H-NMR spectra of the amides **5** or **10**, through the $^3J_{H,H}$ coupling constant values.

However, for the substituted diylides **2b** (R = Me or *n*-Pr) with aldehydes (table 1 : entries 2, 3, 5 ; table 2 : entry 13) or for the unsubstituted diylide **2a** (R = H) with acetophenone (table 1 : entry 7), the assignment becomes harder because the amides **5** or **10** obtained are tri-substituted alkenes for which the allylic coupling constants $^4J_{H,H}$ of the corresponding *E* and *Z* isomers are too close to be significant .[7]

However, ^{13}C-NMR has been used to solve similar attribution problems. [8,9] In particular, Jones *et all* [8] showed that a coupling constant $^3J_{CO,H}$ allows the identification of both *E* and *Z isomers* in the case of aryl substituted α,β-unsaturated ketones and esters. Indeed, the *cis* constant values, in the range of 6 to 8 Hertz, are for all the cases investigated 3 to 5 Hertz lower than the *trans* ones (around 10 to 14 Hertz)(fig 8).



$$\Delta\,{}^3J_{CO,H} = {}^3J^{trans}_{CO,H} - {}^3J^{cis}_{CO,H} = 3 \text{ to } 5 \text{ Hertz}$$

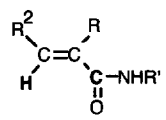
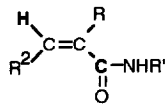
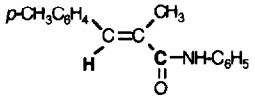
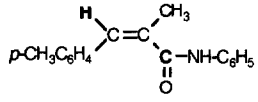
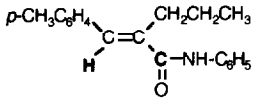
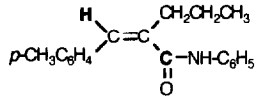
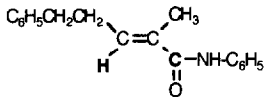
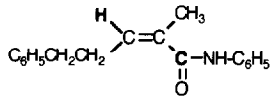
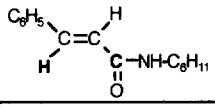
Fig 8

Tri-substituted α,β-unsaturated amides **5** or **10** exhibiting comparable mesomeric effects on the ethylenic bond as those of the two functions studied by Jones, we extrapolated his results for the stereochemical assignments, observing in three cases (**5b**, **5c**, **5e**) a similar difference ($\Delta^3J_{CO,H}$) beetween *Z* and *E* isomers (table 3). The ^{13}C-NMR measurements show the major formation of the *E* isomer.

In one case (amide **5e**) we could check the validity of this method by a ^{1}H-NMR NOE DIFF experiment (another verification of the method was obtained by the $^3J_{H,H}$ and $^3J_{CO,H}$ measurements of a simple disubstituted α,β-unsaturated amide **10l**, both measurements corroborating a *E* isomer).

It is important to note that selective irradiations of the alkyl or amido group hydrogens were necessary to obtain the $^3J_{CO,H}$ coupling constants in the tri-substituted α,β-unsaturated amides spectra. However in two cases (amides **5g** and **10m**) it was not possible to conclude by this method because of the complexity of the spectra even under irradiation. A solution was found for the amide **5g** for which the difference in ^{13}C-NMR measurements beetween $^3J_{CH_3,H}$ (*Trans*)(7.9 Hertz) and $^3J_{CH_3,H}$ (*Cis*) (6.9 Hertz) could be identified, showing the likely formation of the *E* isomer. For the amide **10m** we could only assume that we obtained mainly the *E* isomer on the basis of all our other examples.

Table 3: Carbonyl Chemical Shifts and Coupling Constants in ^{13}C-NMR Spectra of *E* and *Z* Amides **5** or **10** (Determined after Selective Irradiations of the Alkyl or Amido Group Hydrogens).

Amide	 isomer *E*	δ (CO) (ppm)	$^3J_{CO,H}$ (Hz)	 isomer *Z*	δ (CO) (ppm)	$^3J_{CO,H}$ (Hz)
5b		169.0	4.9		169.5	7.8
5c		168.6	4.7		168.8	7.5
5e [a]		168.2	4.2		168.8	6.9
10l [b]		165.5	5.5			

a) Assignment corroborated by a ^{1}H-NMR NOE DIFF experiment. b) assignment corroborated by $^3J_{H,H}$ measurement in ^{1}H-NMR.

The high *E* stereoselectivity observed is not really surprising. Indeed the intermediate phosphonium monoylides **3'** or **8'** involved in the step of amide or amidine double bond formation are of the semi-stabilized class. These type of ylides are known to produce usually mixtures of *Z* and *E* alkenes non stereoselectively, but many factors can influence the *Z*: *E* ratio [10].

The factors enhancing the *E*-stereochemistry may be connected to the ylide itself : so, anionic groups such as carboxamide or carboxylate, for instance, increase greatly the formation of the *E* isomer, probably because of a competitive complexation of these groups with the phosphorus atom [10, 11] : accordingly to that the anionic substituants "NCX$^-$" (X = O or N*c*Hx) on the carbanions of **3'** and **8'** effectively favour the *E* stereochemistry. Moreover, when the phenyl group of the monoylide **1** is replaced in the monoylides **3'** or **8'** by a less sterically bulky and more electron donating alkyl group like CH_2-R, the ratio of *E* isomer is strongly increased . [10-12]

Other factors that may influence the *E* stereochemistry depend either on the character of the carbonyl group, or on the nature of the associated salts. However, it is necessary to be careful since the examples

pointed out in the literature are most often related to the synthesis of disubstituted alkenes but in many of our amide or amidine syntheses, the double bond is actually trisubstituted.

In the case of the semi-stabilized ylide **2c**, the ylides **3** or **8** involved in the Wittig reaction leading to the alkene **6**, are of the semi-stabilized class too. In this case the *E* stereoselectivity observed is also probably connected with the presence of the anionic substituants "NCX$^-$" (X = O or NcHx), which can in this case not only coordinate on the phosphorus atom but also promote a benzylic proton exchange on the intermediate phosphorane in a similar way to the Schlosser modification [13].

Lastly, the *E* stereoselectivity observed in the formation of alkene **6** starting from the stabilized diylide **2d**, directly involved as the Wittig reagent, is in good accordance with the results of the literature for this class of ylide.

Conclusion

The delimitation of the application field of the phosphonium diylides could be settled in their reactivity towards derivatives of carbonic anhydrides. The scope of the reaction is directly depending on the stabilization of the diylides : thus, the non-stabilized diylide **2a** (R = H), **2b** (R = Me, Pr) react with phenylisocyanate and dicyclohexylcarbodiimide (DCC) allowing the *E* stereoselective synthesis of di- or trisubstituted α,β-unsaturated amides or amidines.

The semi-stabilized diylide **2c** (R = Ph) reacts also with the same isocyanate or carbodiimide, but the intermediate adducts **3** or **8**, coupled with aldehydes, give simple alkenes resulting from the Wittig reaction of the remaining benzyl group.

On the contrary, the stabilized diylide **2d** (R = COPh) is inactive towards isocyanates or carbodiimides. It however leads to the *E* stereoselective synthesis of alkenes through a Wittig reaction with the aldehydes introduced in the mixture.

Finally, we can note that, whatever the diylide considered, PhNCO or DCC show a similar behaviour leading to the same families of products.

Probably, the extrapolation of our model study "diylide / carbonic anhydride derivatives" to the reactivity of diylides with other substrates should be possible, the borderline lying likely around the "pivot" behaviour of the semi-stabilized diylide **2c** (R= Ph).

Experimental Section

All experiments were performed under nitrogen by means of the Schlenk technology. Melting points were determined on a Leitz 350 apparatus. NMR spectra were recorded on a Bruker 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. Tetrahydrofuran (THF) was distilled under nitrogen atmosphere over sodium/benzophenone and stored upon sodium.

*General procedure for the synthesis of α,β-unsaturated amides **5** and alkenes **6** from phenylisocyanate.*

Under nitrogen atmosphere, the phosphonium salt [14] (10 mmol) 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, phenylisocyanate (1.08 ml, 10 mmol) in anhydrous THF (50 ml) is slowly added and the solution is refluxed for 24 h. After cooling at room temperature, the carbonyl compound (20 mmol) is added quickly. The reaction was performed at different times and temperatures (see table 1), before acidification with HCl 0.2 N (100 ml). After evaporation of solvent, extraction with CH_2Cl_2 (3 x 80ml), 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 the amide **5** and/or the alkene **6** (eluent : diethyloxide/hexane 6/4). The products are not fully characterized when they are already described in the literature.

α,β-unsaturated Amides 5 .

N-Phenylcinnamamide **5a** [15]

***E** isomer.* mp : 152°C, literature 150-153 °C. IR (KBr) (cm^{-1}) : 3260 (m, NH), 3050 (m),1620 (vs, CO), 1590 (s), 1540 (s), 1490 (s), 1440 (s), 1345 (s), 755 (s). ^{1}H-NMR ($CDCl_3$) : δ = 8.0 (s, 1H, N*H*), 7.78-7.09 (m, 10H, 2 C_6H_5), 7.74 and 6.64 (AB system, 2H, $^3J_{AB}$ = 15.5, C*H*=C*H*). MS (EI, 70 ev) : *m / z* (relative intensity, %) 223 (M^+, 17), 131 (M^+-PhNH, 100), 103 (M^+- PhNHCO, 44), 77 (M^+-PhNHCOCHCH, 28). Anal. calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found : C, 80.82; H, 5.71; N, 6.47.

2-Methyl-N-phenyl-3-(p-tolyl)-prop-2-enamide **5b**

***E** isomer.* mp : 112°C. IR (KBr) (cm^{-1}) : 3275 (m, NH), 1650 (vs, CO), 1620 (s), 1600 (vs), 1540 (vs), 1510 (vs), 1440 (vs), 1325 (s), 780 (m), 700 (s). ^{1}H-NMR ($CDCl_3$) : δ = 7.89 (s, 1H, N*H*), 7.67-7.05 (m, 10H, C*H*= , C_6H_4 and C_6H_5), 2.39 (s, 3H, CH_3-C_6H_4-), 2.18 (d, $^4J_{H,H}$ = 1.3, 3H, CH_3-C=). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 168.3 (*C*O); 138.2, 138.1 (aromatic *C*), 134.3 (*C*H=); 133.0, 132.1 (aromatic*C* and =*C*(CH_3)CO); 129.5, 129.2, 129.0, 124.3, 120.3 (aromatic *C*H); 21.4(*C*H_3); 14.5(*C*H_3) . MS (EI ,70 ev) : *m / z* (relative intensity, %) 251 (M^+, 40), 159 (M^+-PhNH, 100), 131 (M^+-PhNHCO, 95), 91 (M^+-PhNHCOC(CH_3)CH, 42). Anal. calcd. for $C_{17}H_{18}NO$: C, 81.24; H, 6.82; N, 5.57; O, 6.37. found : C, 81.20; H, 6.79; N, 5.70; O, 6.21.

E* + *Z* *isomers (mixture).

^{13}C-NMR ($CDCl_3$, 50.3 MHz) non decoupled : see table **3**. ^{1}H-NMR ($CDCl_3$) : identification of the *Z* isomer (by comparison with the spectra of the isolated *E* isomer): δ = 7.67-7.05 (m, 10H, C*H* = , C_6H_4 and C_6H_5), 6.64 (s, 1H, N*H*), 2.31 (s, 3H, CH_3-C_6H_4-), 2.15 (d, $^4J_{H,CH}$ = 1.6, 3H, CH_3-C=).

N-Phenyl-2-propyl-3-(p-tolyl)-prop-2-enamide **5c**

E* *isomer. IR (KBr) (cm^{-1}) : 3270 (m, NH), 1650 (vs, CO), 1615 (s), 1600 (s), 1510 (s), 1435 (s), 1320 (s). ^{1}H-NMR ($CDCl_3$) : δ = 7.79 (s, 1H, N*H*), 7.66-7.05 (m, 10H, C*H*= , C_6H_4 and C_6H_5), 2.59 (m, 2H, $CH_3CH_2CH_2$), 2.39 (s, 3H, CH_3-C_6H_4), 1.61 (m, 2H, $CH_3CH_2CH_2$), 0.99 (t, 3H, $^3J_{H,H}$ = 7.3, $CH_3CH_2CH_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 168.5 (*C*O); 138.9, 138.2, 138.0 (aromatic *C*); 132.9, 129.2 (aromatic *C*H); 129.1(*C*-CO); 129.0, 128.9, 124.3, 120.1 (aromatic *C*H and H*C*=); 30.2 (CH_2); 22.3 (CH_2); 21.2 (CH_3); 14.2 (CH_3). MS (EI ,70 ev) : *m* / *z* (relative intensity, %) 279 (M^+, 20), 187 (M^+-PhNH, 100), 159 (M^+-PhNHCO, 10), 91 (M^+-PhNHCOC(Pr)CH, 10). Anal. calcd. for $C_{19}H_{21}NO$: C, 81.24; H, 6.82; N, 5.57; O, 6.37. found : C, 81.20; H, 6.79; N, 5.70; O, 6.21.

E* + *Z* *isomers (mixture).

^{13}C-NMR ($CDCl_3$, 50.3 MHz) non decoupled : see table **3**. ^{1}H-NMR ($CDCl_3$) : identification of the Z isomer (by comparison with the spectra of the isolated *E* isomer) : δ = 6.60 (s, 1H; N*H*), 7.66-7.05 (m, 10H, C*H*= and C_6H_4 and C_6H_5), 2.47 (m, 2H, $CH_3CH_2CH_2$), 2.31 (s, 3H, CH_3-C_6H_4), 1.58 (m, $CH_3CH_2CH_2$), 0.98 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, $CH_3CH_2CH_2$).

N,5-Diphenylpent-2,4-dienamide **5d** [16]

E* *isomer. mp : 190°C, literature 188-190°C. IR (KBr) (cm^{-1}) : 3290 (m, NH), 1650 (vs, CO), 1610 (s), 1590 (s), 1530 (s), 1485 (s), 1435 (m), 1350 (s), 1250 (s), 1000 (s), 750 (s), 690 (m). ^{1}H-NMR ($CDCl_3$) : δ = 7.61 (s, 1H, N*H*), 7.58-7.10 (m, 11H, 2 C_6H_5 and -C*H*=CH-CO), 6.90 (m, 2H, Ph-C*H*=C*H*), 6.12 (AB system, 1H, $^3J_{AB}$ = 14.9, =C*H*-CO (*E*)). Anal. calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found : C, 81.81; H, 5.85; N, 5.48.

2-Methyl-N,5-diphenylpent-2-enamide **5e**

E* *isomer. mp : 98°C. IR (KBr) (cm^{-1}) : 3200 (m, NH), 1630 (s, CO), 1610 (s), 1570 (s), 1500 (s), 1460 (s), 1410 (m), 1300 (s), 730 (s), 710 (s).^{1}H-NMR ($CDCl_3$) : δ = 7.58-7.05 (m, 10H, 2 C_6H_5), 7.47 (s, 1H, N*H*), 6.45 (tq, 1H, $^3J_{CH,CH_2}$ = 7.2, $^4J_{CH,CH_3}$ = 1.4, -C*H*=C-), 2.78 (t, 2H, $^3J_{CH_2,CH_2}$ = 7.7, Ph-CH_2), 2.52 (td, 2H, $^3J_{CH_2,CH_2}$ = 7.7, $^3J_{CH,CH_2}$ = 7.2, -CH_2-C=), 1.89 (d, 3H, $^4J_{CH,CH_3}$ = 1.4, -C=C-CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ 167.6 (*C*O); 141.2, 138.1 (aromatic *C*); 135.3 (*C*H=C); 132.6 (CH=*C*); 129.0, 128.5, 128.4, 126.2, 124.2, 120.0 (aromatic *C*H); 34.9 (CH_2); 30.3 (CH_2); 12.9 (CH_3). MS (EI ,70 ev) : *m* / *z* (relative intensity, %) 265 (M^+, 22), 173 (M^+-PhNH, 100), 145 (M^+-PhNHCO, 80), 91 (M^+-PhNHCOC(CH_3)$CHCH_2$, 100). Anal. calcd. for $C_{18}H_{19}NO$: C, 81.46; H, 7.22; N, 5.37; O, 6.03. Found : C, 81.31; H, 7.25; N, 5.37; O, 6.22.

***E + Z** isomers* (mixture).

^{13}C-NMR ($CDCl_3$) non decoupled : see table **3**. ^{1}H-NMR ($CDCl_3$) : identification of the Z isomer (by comparison with the spectra of the isolated E isomer) : δ = 7.58-7.05 (m, 10H, 2 C_6H_5), 6.90 (s, 1H, N*H*), 5.61 (tq, 1H, $^3J_{CH,CH_2}$ = 7.6, $^4J_{CH,CH_3}$ = 1.5, -C*H*=C-), 2.78 (t, 2H, $^3J_{CH_2,CH_2}$ = 7.7, Ph-CH_2), 2.54 (td, 2H, $^3J_{CH_2,CH_2}$ = 7.7, $^3J_{CH,CH_2}$ = 7.6, -CH_2-C=), 1.97 (d, 3H, $^4J_{CH,CH_3}$ = 1.5, -C=C-CH_3).

N,3-Diphenylcinnamamide **5f** [17]

mp : 132°C, literature 131°C. IR (KBr) (cm^{-1}) : 3290 (m, NH), 3280 (m), 1650 (vs, CO), 1595 (s), 1545 (s), 1490 (s), 1440 (s), 1315 (s), 760 (m), 700 (s). ^{1}H-NMR ($CDCl_3$) : δ = 7.49-7.03 (m, 16H, 3 C_6H_5 and N*H*), 6.52 (s, 1H, C*H*=). Masse (EI ,70 ev) : *m / z* (relative intensity : %) 299 (M^+; 4); 207 (M^+-PhNH, 100), 179 (M^+-PhNHCO, 27). Anal. calcd. for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found : C, 84.24; H, 5.74; N, 4.62.

3-Methyl-N-phenylcinnamamide **5g** [17]

***E** isomer.* mp : 123°C, literature 121°C. IR (KBr) (cm^{-1}) : 3280 (m, NH), 1650 (vs, CO), 1620 (s), 1595 (s), 1525 (s), 1495 (s), 1440 (s), 755 (s), 740 (s). ^{1}H-NMR ($CDCl_3$) : δ = 7.69 (s, 1H, N*H*), 7.62-7.10 (m, 10H, 2 C_6H_5), 6.19 (q, 1H, $^4J_{H,CH_3}$ = 1.2, C*H*=), 2.61 (d, 3H, $^4J_{H,CH_3}$ = 1.2, CH_3-C=). MS (EI ,70 ev) : *m / z* (relative intensity, %) 237 (M^+, 14); 145 (M^+-PhNH, 100), 117 (M^+-PhNHCO, 29). Anal. calcd. for $C_{16}H_{15}NO$: C 80.98; H 6.37; N 5.90; found : C 80.83; H 6.28; N 5.91.

***E + Z** isomers* (mixture).

^{13}C-NMR ($CDCl_3$) non decoupled : $\Delta\,^3J_{CH_3,H} = {}^3J_{CH_3,H}$ (*Trans*) (7.9 Hz) - $^3J_{CH_3,H}$ (*Cis*) (6.9 Hz) = 1Hz.

^{1}H-NMR ($CDCl_3$) : identification of the *Z* isomer (by comparison with the spectra of the isolated I*E* isomer) : δ = 7.80-6.87 (m, 11H, 2 C_6H_5 and N*H*), 6.07 (q, 1H, $^4J_{H,CH}$ = 1.5, C*H*=), 2.20 (d, 3H, $^4J_{H,CH}$ = 1.5 , CH_3-C=).

2-Methyl-N,3,3-Triphenylcinnamamide **5h**

mp : 173-5°C, IR (KBr) (cm^{-1}) : 3290 (m, NH), 3275 (m), 1660 (vs, CO), 1600 (s), 1545 (s), 1495 (s), 1440 (s), 1325 (m), 750 (s), 700 (s). ^{1}H-NMR ($CDCl_3$) : δ = 7.38-7.03 (m, 15H, 3 C_6H_5), 6.86 (s, 1H, N*H*), 2.14 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 169.6 (*C*O); 143.2, 141.3, 140.9, 137.5, 133.1(aromatic *C* and *C*=); 129.7, 129.1, 128.8, 128.7, 128.3, 128.1, 127.7, 124.4, 120.1 (aromatic CH)18.9 (*C*H_3). MS (EI ,70 ev) : *m / z* (relative intensity, %) 313 (M^+, 13); 221 (M^+-PhNH, 100), 193 (M^+-PhNHCO, 20), 178 (M^+-PhNHCO -CH_3, 30). 115 (M^+-PhNHCO -H -Ph, 61). Anal. calcd. for $C_{22}H_{19}NO$: C 84.32; H 6.11; N 4.47; found : C 84.35; H 6.14; N 4.45.

Alkene 6

p-Methylstilbene (table 1, entry 11 ; table 2, entry 17)[18].

***E** isomer.* mp : 119°C, literature 116-118°C. ^{1}H-NMR ($CDCl_3$, 200 MHz) : δ = 7.61-7.15 (m, 11H, C_6H_5, C_6H_4 and C*H*=C*H*), 2.43 (s, 3H, CH_3-Ph). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 137.6, 137.5, 134.7, 129.5, 128.7, 128.7, 127.8, 127.5, 126.5, 126.4, 21.3 (*C*H_3).

1-Phenyl-3-(p-tolyl)-prop-2-ene-1-one (table 1, entry 10 ; table 2, entry 16)[19].

E isomer. mp : 95°C, literature 96°C. IR (KBr) (cm^{-1}) : 3050, 3020, 2960, 2910, 1650, 1440, 1330, 820. ^1H NMR ($CDCl_3$) : δ = 8.04 and 7.19 (AB system, 4H, $^3J_{AB}$ = 8.0, C_6H_4), 7.78 [AB system part B, 1H, $^3J_{AB}$ = 15.7, C*H*=], 7.55-7.43 (m, 6H, C*H*= and C_6H_5), 2.35 (s, 3H, CH_3-Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 190.4 (*C*O); 144.9 (*p*-tolyl-*C*H=); 141.1, 138.4 (aromatic *C*); 132.7 (aromatic *C*H); 132.2 (aromatic *C*); 129.7, 128.6, 128.5, 127.5 (aromatic *C*H); 121.0 (=*C*-CO); 21.6 (CH_3).

1,1-Diphenylpropene (table 1, entry 8 ; table 2, entry 14).

mp : 50°C, literature [20] 52°C. ^1H NMR ($CDCl_3$) : δ = 7.46 and 7.21 (m 10H, 2 C_6H_5), 6.22 (q, 1H, $^3J_{H,CH_3}$ = 7.0, =C*H*), 1.81 (d, 3H, $^3J_{H,CH_3}$ = 7.0, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$) : δ = 142.9, 142.4, 139.9, 130.0, 128.1, 128.0, 127.1, 126.8, 126.7, 124.1, 15.7 (CH_3).

*General procedure for the synthesis of α,β-unsaturated amidines **9** and amides **10** or alkenes **6** from dicyclohexylcarbodiimide.*

Under nitrogen atmosphere, the phosphonium salt [14] (10 mmol) 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, dicyclohexylcarbodiimide (2.48 ml; 12 mmol) is slowly added in anhydrous THF (50 ml) and the solution is refluxed for 24 h. After cooling at room temperature, the carbonyl compound (20 mmol) is added rapidly and the solution is stirred for 3 days more before acidification with HCl 0.2 N (100 ml; 20 mmol). After evaporation of solvent, extraction with CH_2Cl_2 (3 x 80ml), washing of the organic layer with water and drying over Na_2SO_4, the mixture is concentrated to turn into a crude oil containing the amidine **9** and/or the alkene **6** (GC-MS). So, the oil was added to diglyme (100ml) and NaOH 1.25 N (40 ml, 50 mmol) and heated for 3 days at 100 °C. Then, after neutralization with HCl to pH 7, the solvent is evaporated and the aqueous layer extracted with CH_2Cl_2 (3 x 100ml) and dried over Na_2SO_4. After concentration, the residual oil is purified by chromatography on silica gel (eluent : diethyloxide-hexane 6:4) to give the corresponding amide **10** [the alkenes **6** are also obtained in three cases (entries 14, 16 and 17) ; these products are already described in the previous paragraph].

N-Cyclohexylcinnamamide **10l** [15]

E isomer . mp : 180°C, literature 179-180°C. IR (KBr) (cm^{-1}) : 3270 (s, NH), 2910 (m), 2850 (m), 1650 (vs, CO), 1615 (s), 1550 (s), 1440 (m), 1340 (m), 1215 (m). ^1H-NMR ($CDCl_3$) : δ = 7.52-7.26 (m, 5H, C_6H_5), 7.61 and 6.37 (AB system, 2H, $^3J_{AB}$ = 15.6, C*H*=C*H*), 5.54 (s, 1H, N*H*), 3.92 (m, 1H, N-C*H*), 2.03-1.11 (m, 10H, C_6H_{10}). ^{13}C-NMR ($CDCl_3$) : see table **3**. MS (EI ,70 ev) : *m / z* (relative intensity, %) 229 (M^+, 36); 131 (M^+-*c*Hx-NH, 100), 103 (M^+-*c*HxNHCO, 47), 98 (M^+-PhCH=CHCO, 16), 77 (M^+-*c*HxNHCOCH=CH, 33).

N-Cyclohexyl-2-methyl-3-(4-tolyl)-prop-2-enamide **10m** .

E isomer . mp : 157°C. IR (KBr) (cm^{-1}) : 3290 (s, NH), 2995 (s), 2850 (m), 1640 (vs, CO), 1610 (s), 1530 (s), 1460 (m), 1340 (m), 825 (m),. ^{1}H-NMR($CDCl_3$, 200 MHz) : δ = 7.25-7.13 (m, 5H, C*H*= and C_6H_4), 5.72 (d, 1H, $^3J_{NH,CH}$ = 7.1, N*H*), 3.85 (m, 1H, C*H*-NH), 2.34 (s, 3H, CH_3-C_6H_4), 2.04 (s, 3H, CH_3-C=), 2.01-1.08 (m, 10H, C_6H_{10}). ^{13}C{^{1}H}-NMR ($CDCl_3$) : δ = 168.9 (*C*O); 137.6, 133.4 (aromatic *C*); 133.3 (aromatic *C*H); 131.8 (=*C*-CO); 129.3, 129.0 (aromatic *C*H and *C*H=); 48.6, 33.2, 25.6, 25.0 (cyclohexyl *C*H and CH_2); 21.3 (CH_3); 14.4 (CH_3). MS (EI ,70 ev) : *m / z* (relative intensity, %) 257 (M^+, 58); 174 (M^+-*c*Hx, 100), 159 (M^+-*c*HxNH, 72), 131 (M^+-*c*HxNHCO, 50), 98 (M^+-*p*-tolylCH=C(CH_3)CO, 28), 91 (M^+-*c*HxNHCOC(CH_3)CH, 18). Anal calc for $C_{17}H_{23}NO$: C 79.33; H 9.01; N 5.44; O, 6.22; found : C 79.26; H 8.90; N 5.57; O, 5.81.

Procedure for the synthesis of the benzyldiphenyl[(N-phenylcarbamoyl)benzyl]phosphonium bromide 3"c (R = Ph).

Under nitrogen atmosphere, the dibenzyldiphenylphosphonium bromide (10 mmol) 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, phenylisocyanate (1.08 ml, 10 mmol) in anhydrous THF (50 ml) is slowly added and the solution is refluxed for 24 h. After cooling at 0°C the mixture is hydrolysed with HCl (50 ml, 0.5 N). After evaporation of the solvent under reduced pressure, extraction with $CHCl_3$, drying over Na_2SO_4 and concentration, the residue is separated by column chromatography on silica gel. The phosphorus compound eluted is washed with HCl (20 ml, 0.5N), and affords after recrystallization ($CHCl_3$/EtOAc) the phosphonium salt **3"c**.

mp : 210°C. IR (KBr) (cm^{-1}) : 3160 (m, NH), 3110 (m), 3020 (s), 2930 (s), 1670 (s, CO), 1598 (s), 1550 (s), 1492 (s), 1437 (s), 1431 (s), 1356 (s), 1111 (s), 970 (s), 950 (s), 942 (s), 698 (s), 685 (s). ^{1}H-NMR($CDCl_3$, 200 MHz) : δ = 11.31 (s, 1H, N*H*), 6.6-8.1 (m, 26 H, aromatic C*H* and PC*H*), 4.43 (d, 2H, $^2J_{P,H}$ = 14, CH_2). Anal calc for $C_{33}H_{29}NOPBr$: C 69.96; H 5.12; N 2.47; P, 5.47; found : C 70.05; H 5.20; N 2.35; P, 5.31.

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