Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 17 Sep 2007.

To cite this article: Edgardo N. Durantini (1999) Synthesis of Functional Olefins Using the Wittig-Horner Reaction in Different Media, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:23, 4201-4222

To link to this article: http://dx.doi.org/10.1080/00397919908085894

SYNTHETIC COMMUNICATIONS, 29(23), 4201–4222 (1999)

SYNTHESIS OF FUNCTIONAL OLEFINS USING THE WITTIG-HORNER REACTION IN DIFFERENT MEDIA

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Abstract. A convenient procedure for the synthesis of *E*-olefins bearing electron donor-acceptor groups is reported. A new diethyl N-aryl aminobenzylphosphonate (**1d**) was synthesized. Reactivity of Wittig-Horner reaction is compared. Expansion of the π-conjugate chain involves the reduction of N-methoxy-N-methyl amide to aldehyde by reaction with DIBAL-H.

Molecules bearing an electron acceptor (A) and an electron donor (D) group bonded by a central π-conjugates spacer are interesting materials, which can display nonlinear optical properties.[1] Furthermore, π-conjugate compounds, such as polyene or polyphenylene derivatives have applications in the design of molecular-scale electronic devices.[2] Mainly, the synthesis of these compounds involve the formation of double bond bearing functional substituents that allow to perform a new extension of the conjugate chain. Of the many routes, which have been devised to form a carbon-carbon double bond, the Wittig-Horner reaction is

particularly useful for the synthesis of conjugated dienes and polyenes.[3] Consequently, several aldehydes and phosphonates have been treated in divers reaction media.[4] Particularly, the Wittig-Horner reaction has been carried out using either a solid-liquid two phase system [5] or liquid-liquid phase transfer catalysis (PTC) conditions.[6] In comparable cases, higher yields were reported for the reactions of aldehydes and phosphonates in the liquid-solid two phase system.[7] The stereochemistry of the olefin product is generally *E*-isomer, although the *Z*-isomer could be obtained in some cases.

This paper reports a convenient procedure for the synthesis of olefins bearing an electron donor and electron acceptor group linked by π-conjugated chain. The new double bond was introduced via the Wittig-Horner reaction. Thus, 4-nitro and 4-methoxybenzaldehyde were treated with different activated phosphonates (**1a-e**) (Scheme 2). The reaction rate was compared in two heterogeneous media, liquid-solid two phase system (Method A: THF/$NaCH_3O$) versus PTC conditions (Method B: dichloromethane/aqueous NaOH). The results show that the reaction gives better yields and proceeds more rapidly when method A was used (Table 1). In all cases, the Wittig-Horner reaction afforded 100 % of *E*-isomer except for phosphonate (**1b**) that contain one less hindered -CN group.

For the synthesis of the polyphenyl models (**2e** and **3e**) bearing two different spacers, a double bond and amino group, the unknown N-aryl aminobenzylphosphonate (**1e**) had to be synthesized. A convenient procedure for N-arylation of substituted anilines bearing electron withdrawing groups has been

reported. [8] This involves the S_NAr reaction between the aniline and activated haloaromatic substrates under PTC condition. Therefore, N-arylation reaction between aminobenzyl phosphonate (**1d**) and 1-fluoro-2,4-dinitrobenzene was effectively carried out under solid-liquid two phase catalyzed system using solid KOH at room temperature (Scheme 1).

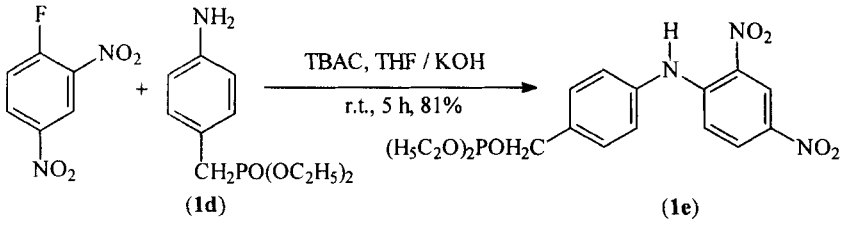
Particularly, the reaction of aldehyde derivatives with diethyl (N-methoxy-N-methylcarbamoyl methyl) phosphonate (**1a**) affords a double bond bearing the N-methoxy-N-methyl amide group. This functional group reacts with DIBAL-H at low temperature to produce a new aldehyde (Scheme 3).[9,10] Thus, this functional amide group was used to allow for extension of the π-conjugate chain in the olefin by a second Wittig-Horner reaction with phosphonate (**1c**).

Phosphonates Formation.

The original observation that alkyl halides react with trialkyl phosphites to give the phosphonate esters was found to be valid for a wide variety of substituents on both reactants.[3,11] Thus, diethyl (4-carbomethoxy) benzylphosphonate **(1c)** was efficiently synthesized by reacting methyl 4-(bromomethyl)benzoate with triethyl phosphite in toluene. The reaction mixture was stirred at reflux for 28h to yield 94 % of pure phosphonate ester (**1c**).

In order to synthesize a polyphenylene compound (**2e**) and (**3e**) containing N-aryl bearing electron withdrawing -NO_2 groups, the previously unknown N-aryl aminobenzyl phosphonate (**1e**) was synthesized. A convenient procedure for this

synthesis can be accomplished by S_NAr reaction between the aromatic substrate with an activated leaving group and the corresponding aniline phosphonate. However, the nucleophilicity of the substituted anilines decreases when the aromatic ring bears electron withdrawing group. On the other hand, aniline NH-acidity is enhanced in these cases. Therefore, the nucleophile can be activated in strongly alkaline media under phase transfer catalysis conditions. Thus, the reaction between diethyl 4-aminobenzylphosphonate (**1d**) and 1-fluoro-2,4-dinitrobenzene was efficiently carried out in THF/KOH solid-liquid PTC system using TBAC as catalyst (Scheme 1).



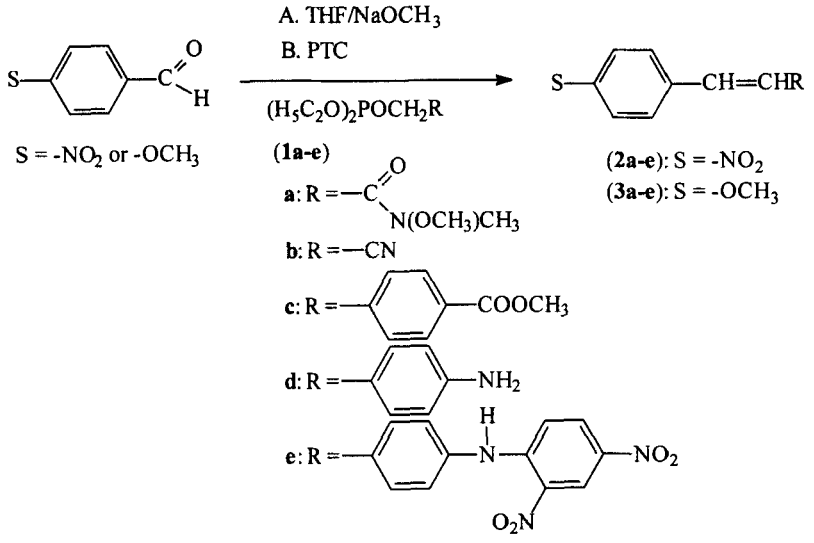
Scheme 1

The reaction mixture was stirred for 5h at room temperature and the resulting *ipso*-fluoro substitution product (**1e**) was obtained with 81% of yield. This method provides a general procedure for the synthesis of N-arylated aniline phosphonates bearing electron withdrawing groups in the N-aromatic ring

Wittig-Horner reactions of *para*-substituted benzylaldehydes with phosphonates in different media.

Scheme 2 illustrates the Wittig-Horner reactions studied and the media

used. These reactions were performed with two different reaction conditions (Method A and Method B).



Scheme 2

Method A involves a solid-liquid heterogeneous medium using THF/sodium methoxide and Method B implies liquid-liquid PTC conditions with dichloromethane as organic solvent in 50% NaOH aqueous solution, using tetrabutylammonium chloride (TBAC) as catalyst. In all cases, the reaction mixtures were efficiently stirred for 20 min. at room temperature.

Two aldehydes with different reactivity were used, 4-nitrobenzaldehyde containing an electron withdrawing nitro group and 4-methoxybenzaldehyde with an electron donor methoxy group, which diminishes the electrophilicity of the C=O bond.[12] To study the scope of the synthetic method, several phosphonates

Table 1. Wittig-Horner reactions between 4-nitrobenzylaldehyde and phosphonates (**1a-e**) under different media at r.t., t=20 min.

Phosphonate	Product	Method A		Method B	
		Yield % [a]	*E*-Isomer % [b]	Yield % [a]	*E*-Isomer % [b]
1a	**2a**	98	100	86	100
1b	**2b**	97	80	91	96
1c	**2c**	95	100	87	100
1d	**2d**	40 [c]	100	18 [c]	100
1e	**2e**	69 [c,d]	100	-	-

[a] Yield of isolated product. Purity >98% as determined by GC analysis. [b] As determined by ^{1}HNMR spectroscopy. [c] After column chromatography on silica gel, using dichloromethane as eluent. [d] Sodium methoxide 500 mg, t=3 h.

(**1a-e**) with different structures were employed. The results are shown in Table 1 and 2 for 4-nitro and 4-methoxybenzaldehyde, respectively.

The aldehyde substrates were selected to provide possibly representative data concerning the utility of these reactions for the preparation of dienes in different conditions. In general for these reactions shown in Scheme 1, better yields are obtained using solid-liquid two phase system (Method A) than with liquid-liquid PTC conditions (Method B). The product can be easily isolated and hydrolysis-sensitive groups, such as -$COOCH_3$, remain intact under these conditions.

The reaction yields depend mainly on the α-CH acidity of the phosphonate (**1a-e**) and on the electrophilicity of the carbonyl reagent. Thus, when acidic

Table 2. Wittig-Horner reactions between 4-methoxybenzylaldehyde with phosphonates (**1a-e**) under different media at r.t., t=20 min.

Phosphonate	Product	Method A		Method B	
		Yield % [a]	*E*-Isomer % [b]	Yield % [a]	*E*-Isomer % [b]
1a	**3a**	97	100	86	100
1b	**3b**	98	92	88	82
1c	**3c**	96	100	75	100
1d	**3d**	NR	-	NR	-
1e	**3e**	56[c,d]	100	-	-

[a] Yield of isolated product. Purity >98% as determined by GC analysis. [b] As determined by ^{1}HNMR spectroscopy. [c] After column chromatography on silica gel, using dichloromethane as eluent. [d] Sodium methoxide 216 mg, t=18 h. NR no reaction.

phosphonates (**1a-c**) were used the reactions proceed with very high yield for both 4-nitro and 4-methoxy aldehydes using Method A (Table 1 and 2). Also, for these phosphonates (**1a-c**) yields >75% were obtained using PTC condition (Method B). However, when diethyl 4-aminobenzyl phosphonate (**1d**) was employed under these conditions, the reaction only takes place with 4-nitrobenzaldehyde to give the expected stilbene (**2d**) with not high yield (Table 1). These results show that the nature of the aromatic ring substituents of the phosphonate influences decisively in the yields of products. Thus, the less acidic phosphonate (**1d**) bears an electron donor 4-amine group, reacts only with pronounced carbonyl reactivity but not with the less activated 4-methoxybenzaldehyde. While phosphonate (**1c**)

contains an electron withdrawing 4-carbomethoxy group reacts with both aldehydes, under these reaction conditions.

With both methods, only *E*-isomer olefins are obtained for phosphonates (**1a**) and (**1c-d**) as determined by ^{1}HNMR spectroscopy. However, a mixture of *E/Z*-isomers, although mainly *E*-isomer, is formed with the more reactive and less hindered phosphonate (**1b**) (R=-CN).[5a,7]

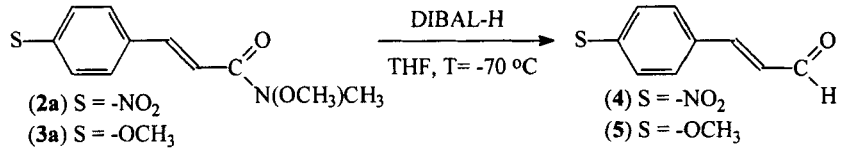
The conversion of stilbene ester (**2c** or **3c**) into aldehyde allows to extend the conjugate chain by a second Wittig-Horner reaction. It can be performed by reduction of stilbene ester with lithium aluminum hydride to alcohol and successive oxidation to aldehyde with MnO_2 in THF.[13]

Particularly, the Wittig-Horner reaction with phosphonate (**1e**) allows to get in one-step the polyphenylene derivative (**2e**) and (**3d**), which contain three phenyl groups bonded by two different spacers, -C=C- and -NH-. These products bear a strong electron withdrawing side with 2,4-dinitrophenyl group.

Reduction of N-methoxy-N-methyl cinnamamide with DIBAL-H.

The conversion of the N-methoxy-N-methyl cinnamamide (**2a**) and (**3a**) into an aldehyde allows for the preparation of the next higher olefine homologue through a second Wittig-Horner reaction. Therefore, amide compounds (**2a**) or (**3a**) were converted into the corresponding aldehyde (**4**) and (**5**) respectively, in one step, by reaction with DIBAL-H in THF at -70 °C (Scheme 3).

These DIBAL-H reduction reactions were carried out at low temperature to prevent further reduction to the alcohol. The results are summarized in Table 3.



Scheme 3

Thus, both amide substrates were easily reduced to aldehyde with very high yield, stirring the reaction mixture for 20 min. at -70 °C. (100% conversion, 98% yield of isolated aldehyde product (**4**) or (**5**)).

Wittig-Horner reaction of cinnamaldehyde (4) and (5) with phosphonate (1c) in different media.

A second Wittig-Horner reaction of cinnamaldehyde (**4**) and (**5**) with diethyl (4-carbomethoxy) benzylphosphonate (**1c**) affords 1,4-substituted 1,3-butadiene (**6**) and (**7**), respectively (Scheme 4).

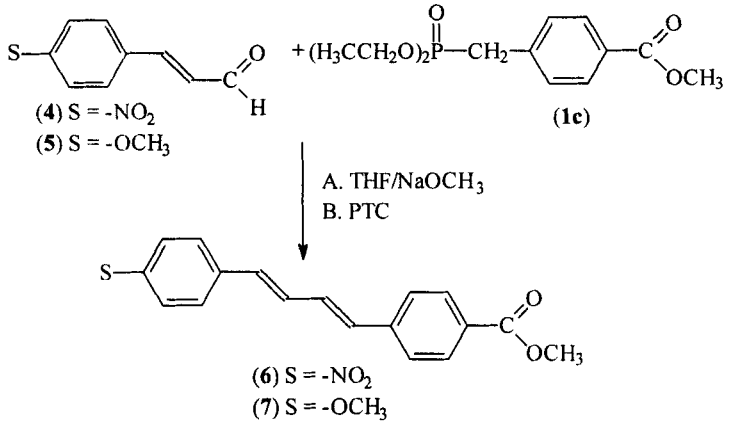
The reaction was carried out using both methods, A and B. The results are shown in Table 4. As can be observed a higher yield was obtained when method A was used. This trend coincides with those found above for the Wittig-Horner reactions shown in Scheme 1.

This reaction involving substituted benzylphosphonate, such as phosphonate (**1c**), allows extending the π-conjugate chain between two substituted phenyl groups. Particularly, the 4-carboxyphenyl group is useful as it can be reduced to an aldehyde or hydrolyzed to the acid ready for another Wittig-Horner reaction or an amide forming coupling reaction, respectively.[13]

Table 3. Reaction of N-methoxy-N-methyl cinnamamide (**2a**) and (**3a**) with DIBAL-H at -70 °C.

Cinnamamide	Cinnamaldehyde	Yield % [a]	*E*-Isomer % [b]
2a	**4**	98	100
3a	**5**	98	100

[a] Yield of isolated product. Purity >98% as determined by GC analysis. [b] As determined by ^{1}HNMR spectroscopy. Reaction time: 20 min.



Scheme 4

Table 4. Reaction of cinnamaldehyde (**4**) and (**5**) with phosphonate (**1c**) under different media at r.t., t=20 min.

Cinnamaldehyde	Product	Method A		Method B	
		Yield % [a]	*E*-Isomer % [b]	Yield % [a]	*E*-Isomer % [b]
4	**6**	96	100	88	100
5	**7**	97	100	81	100

[a] Yield of isolated product. Purity >98% as determined by GC analysis. [b] As determined by ^{1}HNMR spectroscopy.

Therefore, this present strategy could be easily used for the preparation of structurally similar polyphenylene derivatives containing functional groups with electron donor-acceptor properties in both sides of the chain.

Experimental Section

General. Absorption spectra were recorded on a Shimadzu UV-2401PC. NMR spectra were recorded on a Varian Gemini spectrometer at 300 MHz. Mass spectra were taken with a Varian Matt 312 opering in EI mode at 70 eV. TLC Uniplate Silica gel GHLF, 250 microns, thin layer chromatography plates, from Analtech and silica gel 200-400 mesh for column chromatography from Aldrich were used. MS-GC Hewlett Packard 5890 Gas Chromatograph, 5972 Mass Selective detector, Column HP-5 (Crosslinked 5% PH ME Silicone, 30 m x 0.32 mm) was used in chromatography analysis.

Starting materials. Methyl 4-(bromomethyl)benzoate, triethyl phosphite, 4-nitrobenzylaldehyde, 4-methoxybenzylaldehyde, tetrabutylammonium chloride (TBAC), 1-fluoro-2,4-dinitrobenzene, diethyl (N-methoxy-N-methylcarbamoyl methyl) phosphonate, diethyl cyanomethylphosphonate, diisobutylaluminum hydride (DIBAL-H), sodium methoxide (powder) and sodium hydroxide (pellets) from Aldrich; diethyl 4-aminobenzylphosphonate from Fisher were used without further purification. Tetrahydrofuran (THF) from Merck was distilled from lithium aluminum hydride under an argon atmosphere. Dichloromethane (GR grade) from Merck was distilled and storage over 4Å molecule sieves.

Synthesis of phosphonates

Preparation of diethyl (4-carbomethoxy)benzylphosphonate (1c). Methyl 4-

(bromomethyl)benzoate (5.00 g, 21.8 mmol) and triethyl phosphite (6.51 g, 39.2 mmol) in toluene (50 mL) were stirred under a stream of argon. The mixture was heated at reflux for 28 h. The solvent was distilled under reduced pressure and the residue was purified by flash chromatography (dichloromethane/gradient methanol, 5%) to afford 5.87 g (94%) of pure phosphonate (**1c**) as determined by NMR spectroscopy. **UV** λ_{max} (dichloromethane) [nm] (ε [$dm^3mol^{-1}cm^{-1}$]) 236 ($1.75x10^4$), 270 ($1.28x10^3$). ^{1}**HNMR** ($CDCl_3$, TMS) δ 1.23 (t, 6H, J=7.2Hz); 3.19 (d, 2H, J=21.9Hz); 3.90 (s, 3H); 4.02 (q, 4H, J=7.2Hz); 7.36 (d, 2H, J=8.1Hz); 7.98 (d, 2H, J=8.1Hz). ^{13}**CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 16.31 (d, J_{POCC}=5.4Hz, $-CH_3$); 34.00 (d, J_{PC}=138.5Hz, $-OPCH_2-$); 52.06 ($-OCH_3$); 62.25 (d, J_{POC}=7.6Hz, $-CH_2OPO-$); 128.78 ($1C_{Ar}$); 129.75 ($2CH_{Ar}$); 129.84 (d, $J_{PCH_2C_{Ar}C_{Ar}}$=6.4Hz, $2CH_{Ar}$); 137.17 (d, $J_{PCH_2C_{Ar}}$=8.6Hz, $1C_{Ar}$); 166.88 ($-COOCH_3$). **MS** [m/z] 286.1 (M^+).

Preparation of diethyl N-(2,4-dinitrophenyl)-4-aminobenzylphosphonate (1.e). A solution of 1-fluoro-2,4-dinitrobenzene (94.8 mg, 0.51 mmol), diethyl 4-aminobenzylphosphonate (124.0 mg, 0.51 mmol) and TBAC (28 mg, 0.10 mmol) in 10 mL of THF was stirred with 500 mg KOH for 5 h at room temperature. The crude product was neutralized with ammonium chloride solution, washed with water and extracted with dichloromethane. Solvents were removed under reduced pressure and flash chromatography (silica gel, dichloromethane/methanol, 1%) afforded 163 mg (81%) of pure phosphonate (**1e**) as determined by NMR spectroscopy. **UV-visible** λ_{max} (dichloromethane) 358 nm; ε $1.85x10^4$ dm^3mol^-

$^{1}cm^{-1}$. ^{1}**HNMR** ($CDCl_3$, TMS) δ 1.28 (t, 6H, J=7.2Hz); 3.19 (d, 2H, J=22.2Hz); 4.07 (q, 4H, J=7.2Hz); 7.16 (d, 1H, J=9.1Hz); 7.25 (d, 2H, J=8.1Hz); 7.44 (d, 2H, J=8.1Hz); 8.17 (dd, 1H, J=2.7, 9.1Hz); 9.16 (d, 1H, J=2.7Hz); 9.93 (s, 1H, -NH-). ^{13}**CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 16.37 (d, J_{POCC}=5.4Hz, $-CH_3$); 33.34 (d, J_{PC}=138.5Hz, $-OPCH_2-$); 62.21 (d, J_{POC}=6.5Hz, $-CH_2OPO-$); 116.02 ($1CH_{Ar}$); 124.03 ($1CH_{Ar}$); 124.64 ($1C_{Ar}$); 125.45 ($2CH_{Ar}$); 129.89 ($1CH_{Ar}$); 131.10 ($1C_{Ar}$); 131.55 (d, $J_{PCH_2C_{Ar}C_{Ar}}$=6.5Hz, $2CH_{Ar}$); 135.45 (d, $J_{PCH_2C_{Ar}}$=8.4Hz, $1C_{Ar}$); 137.44 ($1C_{Ar}$); 146.96 ($1C_{Ar}$). **MS** [m/z] 409.1 (M^+).

General procedure for the Wittig-Horner reactions.

Method A. A solution of phosphonate (0.30 mmol) and the aldehyde (0.30 mmol) in THF (1 mL) was added to a suspension of sodium methoxide (0.60 mmol) in THF (2 mL). The suspension was stirred for 20 min at room temperature. The crude mixture was neutralized with hydrochloric acid (0.1 N) and then extracted with three portions of dichloromethane (20 mL each). The organic phase was dried with $MgSO_4$, filtered and the solvents removed under reduced pressure. The pure products (**2a-c**) and (**3a-c**) were obtained filtering the residue through a 2 cm diameter x 3 cm plug of silica gel using dichloromethane as solvent. The products (**2d**), (**2e**) and (**3e**) were purified by flash chromatography (silica gel, 1.5 cm diameter x 20 cm) using dichloromethane as eluent. The yields of the pure products are reported above in Table 1 and 2.

Method B. A solution of phosphonate (0.30 mmol), the carbonyl compound (0.30 mmol) and TBAC (0.06 mmol) in dichloromethane (3 mL) was placed in a

cell flask equipped with an efficient mechanic stirrer. After a short period of stirring, 2 mL of a 50% NaOH aqueous solution was added. The mixture was stirred for 20 min at room temperature. The pure products were obtained using the same procedures described above for method A, with the yields reported in Table 1 and 2.

N-Methoxy-N-methyl-4-nitrocinnamamide (2a). UV λ_{max} (dichloromethane) 312 nm; ε 2.51×10^4 $dm^3mol^{-1}cm^{-1}$. ^{1}**HNMR** ($CDCl_3$, TMS) δ 3.33 (s, 3H, $-NCH_3$); 3.79 (s, 3H, $-NOCH_3$); 7.15 (d, 1H, J=15.9Hz, =CH-, *E*-isomer); 7.71 (d, 2H, J=8.7Hz, Ar); 7.76 (d, 1H, J=15.9Hz, =CH-, *E*-isomer); 8.24 (d, 2H, J=8.7Hz, Ar). ^{13}**CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 32.52 ($-NCH_3$); 62.06 ($-NOCH_3$); 120.06 (=CH-; *E*-isomer); 124.10 ($2CH_{Ar}$); 128.59 ($2CH_{Ar}$); 140.56 (=CH-; *E*-isomer); 141.37 ($1C_{Ar}$); 148.24 ($1C_{Ar}$-NO_2); 165.79 (-C=ON-). **MS** [m/z] 236.1 (M^+). Anal. Calcd. for $C_{11}H_{12}N_2O_4$: C 55.92, H 5.12, N 11.86; found C 55.21, H 5.04, N 11.77.

4-Nitrocinnamonitrile (2b). UV λ_{max} (dichloromethane) 298 nm; ε 2.16×10^4 $dm^3mol^{-1}cm^{-1}$. ^{1}**HNMR** ($CDCl_3$, TMS) δ 6.05 (d, 1H, J=16.8Hz, =CH-, *E*-isomer); 7.47 (d, 1H, J=16.8Hz, =CH-, *E*-isomer); 7.63 (d, 2H, J=8.7Hz, Ar); 8.28 (d, 2H, J=8.7Hz, Ar); [5.70 (d, 1H, J=12.3Hz, =CH-, *Z*-isomer); 7.23 (d, 1H, J=12.3Hz, =CH-, *Z*-isomer)]. ^{13}**CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 101.00 (=CH-; *E*-isomer); 116.93 (-CN); 124.36 ($2CH_{Ar}$); 128.11 ($2CH_{Ar}$); 139.15 ($1C_{Ar}$); 147.73 (=CH-; *E*-isomer); 149.05 ($1C_{Ar}$-NO_2); [99.61 (=CH-; *Z*-isomer); 146.02 (=CH-; *Z*-isomer);]. **MS** [m/z] 174.0 (M^+). Anal. Calcd. for $C_9H_6N_2O_2$: C 62.07, H 3.47, N 16.08; found C 62.01, H 3.39, N 16.14.

4'-Carbomethoxy-4-nitrostilbene (2c). UV-visible λ_{max} (dichloromethane) 350 nm; ε $3.67x10^4$ $dm^3mol^{-1}cm^{-1}$. ^{1}**HNMR** ($CDCl_3$, TMS) δ 3.91 (s, 3H, $-COOCH_3$); 7.23 (d, 1H, J=16.5Hz, =CH-, *E*-isomer); 7.30 (d, 1H, J=16.5Hz, =CH-, *E*-isomer); 7.61 (d, 2H, J=8.4Hz, Ar); 7.66 (d, 2H, J=8.7Hz, Ar); 8.06 (d, 2H, J=8.4Hz, Ar); 8.24 (d, 2H, J=8.7Hz, Ar). ^{1}**HNMR** (DMSO-d_6, TMS) δ 3.85 (s, 3H, $-COOCH_3$); 7.56 (d, 1H, J=17.0Hz, =CH-, *E*-isomer); 7.62 (d, 1H, J=17.0Hz, =CH-, *E*-isomer); 7.80 (d, 2H, J=8.4Hz, Ar); 7.90 (d, 2H, J=8.7Hz, Ar); 7.98 (d, 2H, J=8.4Hz, Ar); 8.25 (d, 2H, J=8.7Hz, Ar). ^{13}**CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 52.20 ($-COOCH_3$); 124.21 ($2CH_{Ar}$); 126.86 ($2CH_{Ar}$); 127.19 ($2CH_{Ar}$); 128.70 (=CH-; *E*-isomer); 130.06 ($1C_{Ar}$-$COOCH_3$); 130.17 ($2CH_{Ar}$); 132.05 (=CH-; *E*-isomer); 140.52 ($1C_{Ar}$); 143.17 ($1C_{Ar}$); 147.22 ($1C_{Ar}$-NO_2); 166.62 (Ar-$COOCH_3$). **MS** [m/z] 283.1 (M^+). Anal. Calcd. for $C_{16}H_{13}N_1O_4$: C 67.84, H 4.62, N 4.94; found C 67.92, H 4.57, N 4.88.

4'-Amino-4-nitrostilbene (2d). UV-visible λ_{max} (dichloromethane) 402 nm; ε $2.93x10^4$ $dm^3mol^{-1}cm^{-1}$. ^{1}**HNMR** ($CDCl_3$, TMS) δ 3.86 (s, 2H, $-NH_2$); 6.69 (d, 2H, J=8.1Hz, Ar); 6.94 (d, 1H, J=16.0Hz, =CH-, *E*-isomer); 7.18 (d, 1H, J=16.0Hz, =CH-, *E*-isomer); 7.37 (d, 2H, J=8.1Hz, Ar); 7.56 (d, 2H, J=8.7Hz, Ar); 8.19 (d, 2H, J=8.7Hz, Ar). ^{13}**CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 115.1 ($2CH_{Ar}$); 122.5 (=CH-; *E*-isomer); 124.1 ($2CH_{Ar}$); 126.2 ($2CH_{Ar}$); 128.5 ($2CH_{Ar}$); 130.5 ($1C_{Ar}$); 133.5 (=CH-; *E*-isomer); 140.5 ($1C_{Ar}$); 147.3 ($1C_{Ar}$); 147.8 ($1C_{Ar}$). **MS** [m/z] 240.1 (M^+). Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C 69.99, H 5.03, N 11.66; found C 69.91, H 5.11, N 11.58.

4'-[N-(2,4-Dinitrophenyl)]amino-4-nitrostilbene (2e). UV-visible λ_{max} (dichloromethane) 374 nm; ε $3.30x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 7.10 (d, 1H, J=15.9Hz, =CH-, *E*-isomer); 7.20 (d, 1H, J=15.9Hz, =CH-, *E*-isomer); 7.22 (d, 1H, J=9.0Hz); 7.28 (d, 2H, J=8.1Hz); 7.59 (dd, 2H, J=2.4, 8.7), 7.61 (d, 2H, J=8.1Hz), 8.15 (dd, 1H, J=2.7, 9.0Hz), 8.18 (dd, 2H, J=2.4, 8.7Hz); 9.13 (d, 1H, J=2.7Hz); 9.95 (s, 1H, -NH-). **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 116.16 ($1CH_{Ar}$); 123.82 ($1C_{Ar}$); 124.12 ($1CH_{Ar}$); 124.25 ($2CH_{Ar}$); 124.95 ($1C_{Ar}$); 125.03 ($2CH_{Ar}$); 127.03 ($2CH_{Ar}$); 127.46 (=CH-; *E*-isomer); 128.65 ($2CH_{Ar}$); 129.99 ($1CH_{Ar}$); 130.72 ($1C_{Ar}$); 131.61 (=CH-; *E*-isomer); 135.49 ($1C_{Ar}$); 136.99 ($1C_{Ar}$); 143.28 ($1C_{Ar}$); 146.42 ($1C_{Ar}$);. **MS** [m/z] 406.1 (M^+). Anal. Calcd. for $C_{20}H_{14}N_4O_6$: C 59.11, H 3.47, N 13.79; found C 59.02, H 3.53, N 13.70.

N-Methoxy-N-methyl-4-methoxycinnamamide (3a). UV λ_{max} (dichloromethane) 302 nm; ε $1.85x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 3.28 (s, 3H, $-NCH_3$); 3.74 (s, 3H, $-NOCH_3$); 3.81 (s, 3H, Ar-OCH_3); 6.88 (d, 2H, J=8.7Hz, Ar); 6.89 (d, 1H, J=15.9Hz, =CH-, *E*-isomer); 7.50 (d, 2H, J=8.7Hz, Ar); 7.68 (d, 1H, J=15.9Hz, =CH-, *E*-isomer). **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 32.45 ($-NCH_3$); 55.27 (Ar-OCH_3); 61.72 ($-NOCH_3$); 113.26 (=CH-; *E*-isomer); 114.14 ($2CH_{Ar}$); 127.84 ($1C_{Ar}$); 129.57 ($2CH_{Ar}$); 143.04 (=CH-; *E*-isomer); 161.97 ($1C_{Ar}$-OCH_3); 167.30 (Ar-CON-). **MS** [m/z] 221.1 (M^+). Calcd. for $C_{12}H_{15}N_1O_3$: C 65.14, H 6.83, N 6.33; found C 65.06, H 6.89, N 6.41.

4-Methoxycinnamonitrile (3b). UV λ_{max} (dichloromethane) 308 nm; ε $2.56x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 3.84 (s, 3H, Ar-OCH_3); 5.72

(d, 1H, J=17.1Hz, =CH-, *E*-isomer); 6.92 (d, 2H, J=8.7Hz, Ar); 7.33 (d, 1H, J=17.1Hz, =CH-, *E*-isomer); 7.40 (d, 2H, J=8.7Hz, Ar); [5.28 (d, 1H, J=12.3Hz, =CH-, *Z*-isomer); 7.03 (d, 1H, J=12.3Hz, =CH-, *Z*-isomer)]. **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 55.43 (Ar-OCH_3); 93.38 (=CH-; *E*-isomer); 114.53 ($2CH_{Ar}$); 118.67 (-CN); 126.38 ($1C_{Ar}$); 129.07 ($2CH_{Ar}$); 150.03 (=CH-; *E*-isomer); 162.06 ($1C_{Ar}$-OCH_3); [91.92 (=CH-; *Z*-isomer); 147.71 (=CH-; *Z*-isomer);]. **MS** [m/z] 159.1 (M^+). Anal. Calcd. for $C_{10}H_9N_1O_1$: C 75.45, H 5.70, N 8.80; found C 75.52, H 5.67, N 8.74.

4'-Carbomethoxy-4-methoxystilbene (3c). UV λ_{max} (dichloromethane) 338 nm; ε $4.26x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 3.84 (s, 3H, -OCH_3); 3.91 (s, 3H, -$COOCH_3$); 6.91 (d, 2H, J=8.7Hz, Ar); 6.99 (d, 1H, J=16.5Hz, =CH-, *E*-isomer); 7.14 (d, 1H, J=16.5Hz, =CH-, *E*-isomer); 7.48 (d, 2H, J=8.7Hz, Ar); 7.53 (d, 2H, J=8.4Hz, Ar); 8.01 (d, 2H, J=8.4Hz, Ar). **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 52.01 (-$COOCH_3$); 55.33 (-OCH_3); 114.22 ($2CH_{Ar}$); 125.43 (=CH-; *E*-isomer); 126.01 ($2CH_{Ar}$); 128.08 ($2CH_{Ar}$); 128.45 ($1C_{Ar}$); 129.54 ($1C_{Ar}$); 130.00 ($2CH_{Ar}$); 138.79 (=CH-; *E*-isomer); 142.21 ($1C_{Ar}$); 159.79 ($1C_{Ar}$-OCH_3); 166.94 (Ar-$COOCH_3$). **MS** [m/z] 268.1 (M^+). Anal. Calcd. for $C_{17}H_{16}O_3$: C 76.10, H 6.01; found C 76.17, H 6.10.

4'-[N-(2,4-Dinitrophenyl)]amino-4-methoxystilbene (3e). UV λ_{max} (dichloromethane) 345 nm; ε $2.42x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 3.85 (s, 3H, -OCH_3); 6.92 (d, 2H, J=8.7Hz); 6.98 (d, 1H, J=16.2Hz, =CH-, *E*-isomer); 7.11 (d, 1H, J=16.2Hz, =CH-, *E*-isomer); 7.22 (d, 1H, J=9.1Hz); 7.28 (d,

2H, J=8.1Hz); 7.47 (d, 2H, J=8.7Hz); 7.60 (d, 2H, J=8.1Hz); 8.18 (dd, 1H, J=2.7, 9.1Hz); 9.19 (d, 1H, J=2.7Hz); 9.98 (s, 1H, -NH-). **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 55.38 ($-OCH_3$); 114.26 ($2CH_{Ar}$); 116.19 ($1CH_{Ar}$); 124.13 ($1CH_{Ar}$); 124.40 ($1C_{Ar}$); 124.97 (=CH-; *E*-isomer); 125.47 ($2CH_{Ar}$); 126.90 ($1C_{Ar}$); 127.78 ($2CH_{Ar}$); 127.91 ($2CH_{Ar}$); 129.60 (=CH-; *E*-isomer); 129.91 ($1CH_{Ar}$); 130.72 ($1C_{Ar}$); 135.32 ($1C_{Ar}$); 137.31 ($1C_{Ar}$); 146.97 ($1C_{Ar}$); 164.04 ($1C_{Ar}$-OCH_3). **MS** [m/z] 391.1 (M^+). Anal. Calcd. for $C_{21}H_{17}N_3O_5$: C 64.45, H 4.38, N 10.74; found C 64.36, H 4.43, N 10.66.

General procedure for the reduction with DIBAL-H.

A solution of N-methoxy-N-methyl cinnamamide (**2a**) or (**3a**) (0.2 mmol) in 10 mL of THF was cooled at -70 °C and stirring in an atmosphere of argon. Then, DIBAL-H (71.11 mg, 0.50 mmol in 2mL of THF) was added slowly by drops. The reaction was kept for 20 min at -70 °C. A mixture of 2 mL methanol/water (1:1) was added to eliminate the excess of hydride. The crude product was poured in water and extracted with dichloromethane. The organic extract was dried with $MgSO_4$ and passed through a sintered glass filter containing silica gel. The solvents were evaporated under reduced pressure and the product dried under vacuum to afford the correspondent pure cinnamaldehyde (**4**) or (**5**), respectively. Yields were reported in Table 3.

4-Nitrocinnamaldehyde (4). UV λ_{max} (dichloromethane) 302 nm; ε $2.55x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 6.81 (dd, 1H, J=7.2, 16.5Hz, =CH-COH, *E*-isomer); 7.53 (d, 1H, J=16.5Hz, =CH-, *E*-isomer); 7.73 (d, 2H,

J=8.1Hz); 8.30 (d, 2H, J=8.1Hz, Ar); 9.78 (d, 1H, J=7.2Hz, -COH). **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 124.33 ($2CH_{Ar}$); 129.02 ($2CH_{Ar}$); 131.75 (=CH-; *E*-isomer); 139.72 ($1C_{Ar}$); 146.52 ($1C_{Ar}$); 148.76 (=CH-; *E*-isomer); 192.74 (-COH). **MS** [m/z] 177.0 (M^+). Anal. Calcd. for $C_9H_7N_1O_3$: C 61.02, H 3.98, N 7.91; found C 61.09, H 3.89, N 7.84.

4-Methoxycinnamaldehyde (5). UV λ_{max} (dichloromethane) 318 nm; ε $2.41x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 3.85 (s, 3H, $-OCH_3$); 6.60 (dd, 1H, J=7.8, 15.9Hz, =CH-COH, *E*-isomer); 6.94 (d, 2H, J=8.7Hz); 7.41 (d, 1H, J=15.9Hz, =CH-, *E*-isomer); 7.51 (d, 2H, J=8.7Hz, Ar); 9.64 (d, 1H, J=7.8Hz, -COH). **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 55.40 ($-OCH_3$); 114.52 ($2CH_{Ar}$); 126.49 (=CH-; *E*-isomer); 126.76 ($1C_{Ar}$); 130.30 ($2CH_{Ar}$); 152.64 (=CH-; *E*-isomer); 162.17 ($1C_{Ar}$); 193.63 (-COH). **MS** [m/z] 162.1 (M^+). Anal. Calcd. for $C_{10}H_{10}O_2$: C 74.06, H 6.21; found C 74.14, H 6.15.

Wittig-Horner reaction of cinnamaldehydes with posphonate (1c).

The reactions were performed using the same conditions described previously for heterogeneous Method A. The pure products (**6**) and (**7**) were obtained filtering the residue through a 2 cm diameter x 3 cm plug of silica gel using dichloromethane as solvent. The yields of (**6**) and (**7**) were reported in Table 4.

1-(4-Carbomethoxyphenyl)-4-(4-nitrophenyl)-1,3-butadiene (6). UV-visible λ_{max} (dichloromethane) 378 nm; ε $4.92x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 3.92 (s, 3H, $-COOCH_3$); 6.77 (d, 1H, 15.6 Hz, =CH-, *E*-isomer); 6.82 (d,

1H, J=15.6 Hz, =CH-, *E*-isomer); 7.07 (m, dd, 2H, =CH-CH=, J=10.0, 15.6Hz), 7.52 (d, 2H, J=8.4Hz); 7.57 (d, 2H, J=8.7Hz); 8.02 (d, 2H, J=8.4Hz); 8.20 (d, 2H, J=8.7Hz). **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 52.14 (-$COOCH_3$); 124.18 (2CH_{Ar}); 126.53 (2CH_{Ar}); 126.86 (2CH_{Ar}); 130.09 (2CH_{Ar}); 130.67 (1C_{Ar}); 131.65 (=CH-; *E*-isomer); 133.17 (=CH-; *E*-isomer); 134.66 (=CH-; *E*-isomer); 134.73 (=CH-; *E*-isomer); 141.10 (1C_{Ar}); 145.74 (1C_{Ar}); 149.88 (1C_{Ar}); 163.18 (Ar-$COOCH_3$). **MS** [m/z] 309.1 (M^+). Anal. Calcd. for $C_{18}H_{15}N_1O_4$: C 69.89, H 4.89, N 4.53; found C 69.80, H 4.95, N 4.47.

1-(4-Carbomethoxyphenyl)-4-(4-methoxyphenyl)-1,3-butadiene (7). UV-visible λ_{max} (dichloromethane) [nm] 360 nm; ε $5.51x10^4$ $dm^3mol^{-1}cm^{-1}$. **^{1}HNMR** ($CDCl_3$, TMS) δ 3.83 (s, 3H, -OCH_3); 3.91 (s, 3H, -$COOCH_3$); 6.63 (d, 1H, J=16.0Hz, =CH-, *E*-isomer); 6.69 (d, 1H, J=16.0Hz, =CH-, *E*-isomer); 6.84 (dd, 1H, =CH-CH=, J=9.9, 16.0Hz); 6.88 (d, 2H, J=8.7Hz); 7.04 (dd, 1H, J=9.9, 16.0Hz, =CH-CH=, *E*-isomer); 7.39 (d, 2H, J=8.7Hz); 7.47 (d, 2H, J=8.5Hz); 7.98 (d, 2H, J=8.5Hz). **^{13}CNMR** (75.45 MHz, $CDCl_3$, TMS) δ 52.00 (-$COOCH_3$); 55.33 (-OCH_3); 114.22 (2CH_{Ar}); 126.22 (2CH_{Ar}); 126.77 (=CH-; *E*-isomer); 127.86 (2CH_{Ar}); 128.52 (1C_{Ar}); 129.82 (1C_{Ar}); 129.99 (2CH_{Ar}); 130.37 (=CH-; *E*-isomer); 132.10 (=CH-; *E*-isomer); 134.19 (=CH-; *E*-isomer); 142.12 (1C_{Ar}); 159.62 (1C_{Ar}); 166.91 (Ar-$COOCH_3$). **MS** [m/z] 294.1 (M^+). Anal. Calcd. for $C_{19}H_{18}O_3$: C 77.53, H 6.16; found C 77.61, H 6.09.

Acknowledgments

Author is grateful to Consejo Nacional de Investigaciones Científicas y

Técnicas (CONICET) and Fundación Antorchas (A-13561/1-8) for finalcial support.

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(Received in the USA 16 April 1999)