Heteroatom Chemistry
Volume 10, Number 1, 1999

Use of $Ph_3P=N$-Li: Synthesis of α,β-Unsaturated Nitriles from α,β-Unsaturated Esters via the Formation of N-(α,β-Unsaturated Acyl) Phosphinimines

Henri-Jean Cristau, Amer Hammami, and Eliane Torreilles

Laboratoire de Chimie Organique E. N. S. C. M. (ESA 5076 du C.N.R.S.), 8, Rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France

Received 21 April 1998; revised 23 June 1998

ABSTRACT: *The reaction of $Ph_3P=NLi$ with various α,β-unsaturated esters gives access to new N-(α,β-unsaturated acyl) phosphinimines, which can undergo intramolecular aza-Wittig reactions (at 65–110°C) to afford the corresponding nitriles. The structures of all new compounds were established by elementary analyses, IR, ^1H-, ^{13}C-, and ^{31}P-NMR spectroscopy.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 49–54, 1999

INTRODUCTION

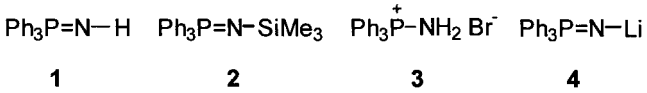
Among the reported methods to create N-acylphosphinimines, the more useful ones are the reactions involving (1) Ph_3P and appropriate acylazides [1,2], amides [3], or N,N-dichloro-urethanes [4]; (2) acid chlorides and phosphinimines **1** [5] or N-silylphosphinimines **2** [6] derived from the aminophosphonium salt **3**; and (3) the salt **3** in the presence of triethylamine and acid chlorides [7]. However, the last two methods require the use of activated acylating reagents. Consequently, we investigated the ability of the lithiated compound **4**, which is a more nucleophilic agent than **1** or **2**, to give N-acylphosphinimines from less reactive electrophilic agents, such as esters (see Scheme 1).

In an earlier study [8,9], **4** has been transformed in high yields into the corresponding N-acylphosphinimine **6** or N-(carbalkoxy)-phosphinimine **8** by reaction with acetyl and benzoyl chlorides **5** respectively, or with some chloroformates **7** (Scheme 2).

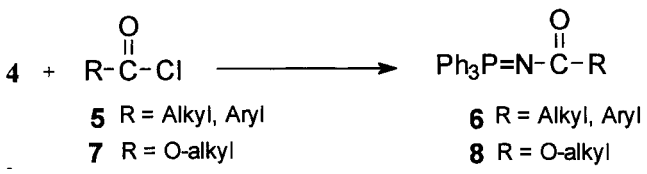
 CCC 1042-7163/99/010049-06

RESULTS AND DISCUSSION

The present work extends further our investigations of the reactions of **4** with esters **9** (Table 1), **11**, and **14** (Table 2). First, it must be noted that, under the experimental conditions used (THF, 40–65°C), **1** does not react with esters. On the contrary, the lithiated imine **4** reacts with most of the esters **9**, at 40°C: A nucleophilic substitution at the carbonyl group affords, as indicated in Table 1, the corresponding new

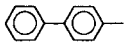


SCHEME 1



SCHEME 2

TABLE 1 Synthesis of Compounds **10** from the Reaction of **4** with Esters **9**

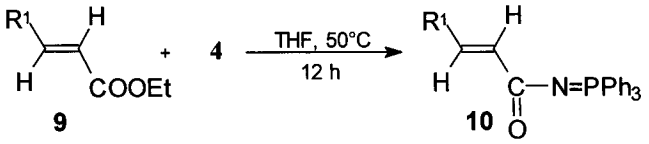
Entry	R_1	**10**	*Tf*[a]	*Yld*[b]
1	Me	**10a**	35	31
2	Et	**10b**	28	25
3	$PhCH_2$	**10c**	-	-
4		**10d**	86	81
5	Ph	**10e**	96	75
6		**10f**	80	53
7		**10g**	51	49
8		**10h**	39	32

[a]Calculated formation (%) from ^{31}P-NMR spectrum, the rest being **1**.
[b]Yield of isolated product (%), based on **9**.

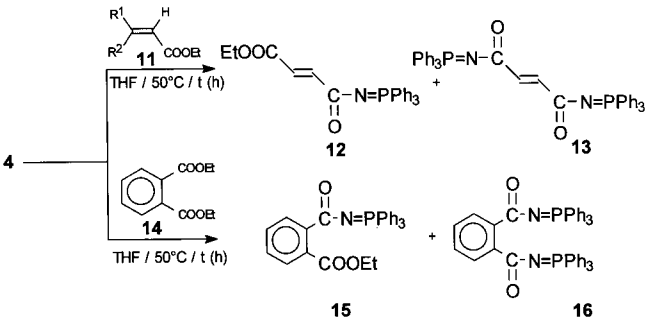
TABLE 2 Reaction of **4** with Some Diesters

Entry		R^1	R^2	n[a]	t(*h*)	**12,15** *Tf*[b] (*Yld*)	**13,16** *Tf*[b] (*Yld*)[c]
	11a					100.0	—
9		H	COOEt	1.0	10	(78.0)	—
	11b					100.0	—
10		COOEt	H	1.0	3	(72.2)	—
	11a					—	46
11		H	COOEt	0.5	3		(40)
	11b					—	54.0
12		COOEt	H	0.5	5		(51.8)
	14					58.5	19.5
13		—	—	1.0	1	(55.4)	(17)
	14					13	67
14		—	—	0.5	1	(10)	(58.7)

[a][Ester]/[**4**] = *n*.
[b]Calculated formation (%) from ^{31}P-NMR spectrum, the rest being **1.**
[c]Yield of the isolated compound (%) based on the starting salt **3**.



SCHEME 3



SCHEME 4

N-acylated phosphinimines, isolated and clearly identified by ^{13}C-, ^{1}H-, and ^{31}P-NMR spectroscopy. The hardness of the nucleophile **4** is well demonstrated by its reactivity with the α,β-unsaturated esters **9**, occurring at the carboxylate group rather than at the β-vinylic carbon (Scheme 3).

In some instances, the yields are not as good as expected, substantial amounts of phosphinimine **1** being detected. The presence of **1** may be explained, in the case of the "vinylogous" enolizable esters, by the presence of an acidic proton at the γ position to the carboxylate group. This protonation of **4** to give **1** occurred quantitatively (100%) when the ester was ethyl 3-benzylacrylate (entry 3). The extent of the protonation was about 65, or 72%, for the 3-methyl- and 3-ethylacrylates (entries 1 and 2) respectively. In the other examples, the protonation (to a lower extent) may result from reaction with the solvent, as observed in a control experiment: The lithiated imine **4** is, in THF solution, transformed slowly into **1** (40% yield, at 50°C after 10 h).

The stability of the resulting phosphinimines **10** depends on the temperature as subsequently emphasized. Therefore, care must be taken to pay close attention to the given experimental conditions.

With the diesters **11** or **14** (Table 2), it is possible to control the extent of mono- as against diacylation reactions. Thus, using a ratio [diester]/[**4**] = 1, the same monosubstitution compound **12** is obtained in satisfactory yields by coupling **4** with diethyl maleate **11a** or with diethyl fumarate **11b** (entries 9 and 10). The isomerization of **11a** into **11b** [10] cannot be avoided (Scheme 4).

Under the same conditions, the diethyl phthalate **14** is converted into the monoester **15** together with compounds **16** and **1**. The monoester **15** can be isolated in pure form by column chromatography.

When the ratio [ester]/[**4**] = 1/2 was employed, double substitution by the phosphinimine group prevailed. In the case of diethyl fumarate **11b**, both the disubstituted product **13** (54%) and the phosphinimine **1** were formed and isolated in pure form. The same compound **13** was also obtained starting from diethyl maleate (entry 11). From diethyl phthalate, a mixture of phosphinimines **1** (20%), **15** (13%), and **16** (67%) was obtained; the main product could then be isolated in pure form. The formation

of compound **1**, in some experiments, can be explained by the protonation of **4** by the solvent. All the new compounds **12**, **13**, **15**, and **16** gave spectra in good agreement with the proposed structures.

SYNTHESIS OF α,β-UNSATURATED NITRILES

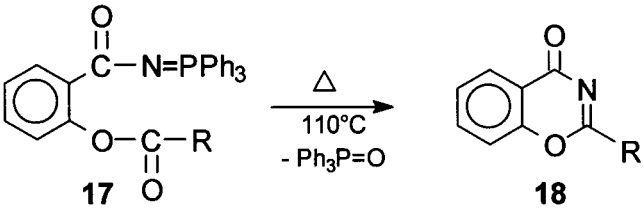
The thermal instability of N-acyl phosphinimines is well known [1]. In the case of Ar-C(O)-N=PPh_3, the normal decomposition, into the corresponding nitrile Ar–CN, takes place at about 200°C. However, starting from salicylic derivatives **17**, nitrile formation is superseded, even at 110°C, by an intramolecular aza-Wittig reaction affording the corresponding benzoxazinones **18** (Scheme 5) [11]. However, cyclization does not occur in the case of lactic acid derivatives **19**, which are converted at 250°C into the α-acetoxynitriles **20** (Scheme 6).

Consequently, we investigated the possibility of intermolecular aza-Wittig reactions, at 65°C, of N-cinnamoyl triphenylphosphinimines **10e** with cinnamaldehyde, or of N-crotonoyl triphenylphosphinimine **10a** with a better candidate, *p*-nitrobenzaldehyde. Triphenylphosphine oxide was obtained, but it resulted from an intramolecular elimination reaction and not, as expected, from an intermolecular aza-Wittig reaction: The corresponding α,β-unsaturated nitriles **21** were isolated from the reaction mixtures by flash chromatography and were well characterized.

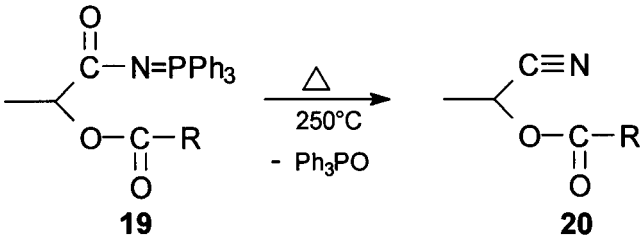
Monitoring by ^{31}P-NMR spectroscopy the heating of the N-acylphosphinimines, we observed the transformation of the N-crotonoyl phosphinimine **10a** into the corresponding nitrile **21a** after 3 hours at 65°C, in THF. On the other hand, the transformation of most of the derivatives **10**, **12**, **13**, **15**, and **16** (Scheme 7), was carried out, in refluxing toluene, at 110°C as reported in Table 3.

It can be pointed out that the diphosphinimines **13** and **16**, under these conditions, only underwent a monoelimination, giving rise to the corresponding monocyanophosphinimines **21i** and **23b**. On operating at higher temperature, at 140°C in DMSO, the double-elimination reactions were achieved, affording 100% yields of the corresponding dinitriles, as, for example, in the case of compound **16**, the 1,2-dicyanobenzene. When the isolated intermediate **23b** was warmed in DMSO at 140°C, the same result was observed.

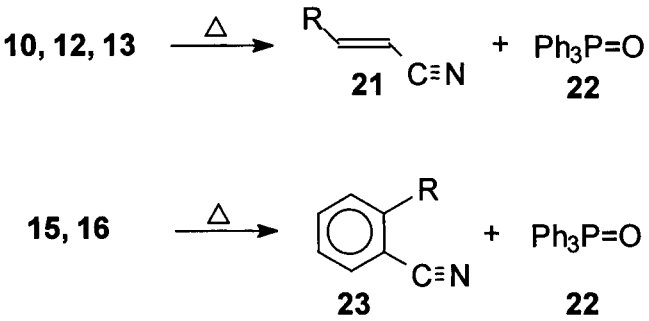
Synthesis of nitriles in this way may be even more interesting, as a "one-pot" process, starting from the aminophosphonium salt **3**. The different



SCHEME 5



SCHEME 6



SCHEME 7

TABLE 3 Thermal Degradation of the N-Acylphosphinimines into Nitriles

N-acyl phosphinimine	*R*	*t(h)*	*T°C*	*Solvent*		*Yld*[a]	**22**[b]	*Ref*[c]
10	Me	3	65	THF	**21a**	93	100	[12]
10	Et	10	65	THF	**21b**	87	96	[13]
10		72	110	toluene	**21c**	89	93	[14]
10	Ph	120	110	toluene	**21d**	78	82	[15]
10		72	110	toluene	**21e**	89	93	[16]
10		72	110	toluene	**21f**	78	80	[17]
10		48	110	toluene	**21g**	79	87	[18]
12	EtO(O)C	72	110	toluene	**21h**	81	95	[19]
13	Ph_3P=NC(O)	48	110	toluene	**21i**	73	85	-
15	COOEt	48	110	toluene	**23a**	79	92	[19]
16	C(O)N=PPh_3	48	110	toluene	**23b**	86	91	-

[a]Isolated yields (%).
[b]Calculated formation (%) from ^{31}P-NMR spectrum.
[c]Identical mp. and spectroscopic characteristics to those reported in the corresponding references.

stages of the reaction were followed by ^{31}P-NMR spectroscopy: (1) addition of *n*-BuLi and then of the ester (Table 4) to a suspension of **3** in THF; (2) warming, at 50°C, of the mixture, the solvent, then being distilled off and replaced by toluene; (3) finally, heating the resulting solution under reflux. The pure nitrile was, in all cases, isolated by simple flash chromatography.

The comparison of Tables 3 and 4 indicates that the one-pot reaction gives comparable overall results with the stepwise synthesis, but, in the one-pot process, the purification of the nitrile is more troublesome, and consequently, the yields are somewhat lower.

In conclusion, use of **4** affords a good way to transform esters into the corresponding nitriles.

Experimental

All manipulations were carried out under an inert atmosphere. Unless otherwise indicated, the ^{1}H-, ^{31}P-, and ^{13}C-NMR spectra were recorded respectively at 200, 50, and 81 MHz on a Bruker AC 200 spectrometer. Chemical shifts (δ) are reported downfield from tetramethylsilane (TMS) for ^{1}H-NMR and ^{13}C-NMR spectroscopy and from external H_3PO_4 (85%) for ^{31}P-NMR spectroscopy. All melting points were uncorrected. The IR of solids (in KBr) and liquids (film) were recorded on a Perkin-Elmer 377 spectrophotometer. Purifications were carried by column chromatography using SDS silica gel 60 A C.C.

The aminophosphonium salt **3** was prepared by the published procedure [9]. This compound was converted into **1** and **4** as reported [9].

N-Substituted Phosphinimines **10, 12, 13, 15,** *and* **16**

Each ethyl ester **9, 11,** or **14** (4.2 mmol) was added to a 50 mL dry THF solution of **4** (4.2 mmol) [prepared in situ from **1** (1.5 g, 4.2 mmol) [9]], at 20°C under a nitrogen atmosphere. The mixture was warmed to 50°C for the time indicated in Tables 1 and 2. The solvent was then removed under reduced pressure, and the residue was washed with 30 mL of cold water. The organic layer was separated, and the aqueous layer was extracted three times with CH_2Cl_2 (25 mL). The organic phase was dried with Na_2SO_4 and concentrated. The organic residue was purified by chromatography (Et_2O/CH_2Cl_2, 1/1).

TABLE 4 One-Pot Formation of Nitriles **21** and **23** from α,β-Unsaturated Esters and the Lithiated Imine **4** (Scheme 5)

Ester	*R*	*[Ester]/[**4**]*	*t*(*h*)	*T* (°*C*)	*Solvent*		*Yld*[a]	**22**[b]
9a	Me	1/1	24	65	THF	**21a**	18	23
11a	COOEt	1/1	72	110	toluene	**21h**	68	96
11a	COOEt	1/2	72	110	toluene	**21i**	39	53
14	COOEt	1/2	48	110	toluene	**23b**	43	52

[a]Yield of pure isolated compound (%).
[b]Calculated formation (%) from ^{31}P-NMR spectrum.

N-Crotonyl Triphenyphosphinimine **10a.** This compound was obtained as a yellow powder. Mp 121°C. IR (KBr), 2960, 2925, 1725, 1645, 1370 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.85 (dd, ^{1}J = 6.81 Hz, ^{2}J = 1.64 Hz, 3H, CH_3), 6.25 (qd, ^{1}J = 15.26 Hz, ^{2}J = 1.68 Hz, 1H, CH=), 6.90 (qd, ^{1}J = 15.27 Hz, ^{2}J = 6.79 Hz, 1H, CH=), 7.20–8.10 (m, 15H, aromatics); ^{13}C NMR ($CDCl_3$), δ = 17.59 (s, CH_3), 128.38 (d, $^{1}J_{PCi}$ = 99.13 Hz), 128.61 (d, $^{2}J_{PCo}$ = 12.27 Hz), 131.68 (s), 132.12 (d, $^{4}J_{PCp}$ = 2.21 Hz), 133.09 (d, $^{3}J_{PCm}$ = 9.86 Hz), 138.49 (d, $^{4}J_{PC}$ = 3.47 Hz), 177.13 (d, $^{2}J_{PC}$ = 8.45 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 21.57. Anal. calcd for $C_{22}H_{20}NOP$: C, 76.49; H, 5.84; N, 4.06; found: C, 76.45; H, 5.82; N, 4.00%; FAB^{+}(70 eV) m/z; found, M+H$^{]+}$ = 346, calcd for $C_{22}H_{20}NOP$; M = 345.128.

trans-N-[1-Oxopenten-2-yl]-triphenylphosphinimine **10b.** This compound was obtained as a yellow oil. IR (film), 3040, 2975, 2920, 1720, 1645, 1550, 1480, 1430, 1350, 1280, 1120, 1030, 970, 860, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.1 (t, CH_3, 3H, ^{1}J = 7.45 Hz), 2.2 (qd, ^{1}J = 7.50 Hz, 2H, CH_2), 6.2 (td, ^{1}J = 15.39 Hz, ^{2}J = 1.53 Hz, 1H, CH=), 6.9 (td, ^{1}J = 15.41 Hz, ^{2}J = 6.77 Hz, 1H, CH=); ^{13}C NMR ($CDCl_3$), δ = 12.66 (s, CH_3), 25.01 (s, CH_2), 128.32 (d, $^{1}J_{PCi}$ = 99.01 Hz), 128.62 (d, $^{2}J_{PCo}$ = 12.27 Hz), 129.29 (d, $^{3}J_{PC}$ = 22.14 Hz), 132.13 (d, $^{4}J_{PCp}$ = 2.51 Hz), 133.10 (d, $^{3}J_{PCm}$ = 9.81 Hz), 144.94 (d, $^{4}J_{PC}$ = 3.52 Hz), 177.30 (d, $^{2}J_{PC}$ = 8.50 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 21.21.

trans-N-[1-Oxo-3-(4'-biphenyl)propen-2-yl]-triphenylphosphinimine **10d.** This compound was obtained as a pale yellow powder. Mp 161°C. IR (KBr), 3040, 3020, 1630, 1560, 1480, 1430, 1340, 1235, 1105, 895, 840, 770, 740, 720, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 6.9 (dd, ^{1}J = 15.78 Hz, ^{2}J = 2.61 Hz, 1H, CH=), 7.3–7.9 (m, 25H, aromatics); ^{13}C NMR ($CDCl_3$), δ = 127.14 (s), 127.45 (s), 127.90 (s), 128.27 (s), 128.37 (d, $^{1}J_{PCi}$ = 99.13 Hz), 128.72 (d, $^{2}J_{PCo}$ = 12.17 Hz), 129.19 (s), 132.25 (d, $^{4}J_{PCp}$ = 2.51 Hz), 133.17 (d, $^{3}J_{PCm}$ = 9.86 Hz), 135.15 (s), 139.27 (d, $^{4}J_{PC}$ = 3.77 Hz), 140.61 (s), 141.48 (s), 176.98 (d, $^{2}J_{PC}$ = 8.25 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 19.88. Anal. calcd for $C_{33}H_{24}NOP$: C, 81.98; H, 5.40; N, 2.89; found: C, 81.94; H, 5.61; N, 2.94; FAB^{+}(70 eV) m/z; found, [M]$^{+}$ = 483 calcd for $C_{22}H_{20}NOP$; M = 483.17.

trans-N-Cinnamoyl triphenylphosphinimine **10e.** This compound was obtained as a yellow oil. IR (film), 3040, 3010, 1680, 1630, 1580, 1550, 1490, 1480, 1430, 1230, 1110, 1080, 1030, 890, 830, 770, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.89 (d, ^1J = 18.60 Hz, 1H, CH=), 7.15 (d, J = 18.61 Hz, 1H, CH=), 7.3–7.8 (m, 20H, aromatics); ^{13}C NMR ($CDCl_3$), δ = 119.53 (s), 127.79 (s), 128.19 (d, $^1J_{PCi}$ = 99.13 Hz), 128.38 (s), 128.69 (d, $^2J_{PCo}$ = 12.32 Hz), 128.87 (s), 131.96 (s), 132.22 (d, $^4J_{PCP}$ = 2.71 Hz), 133.13 (d, $^3J_{PCm}$ = 9.91 Hz), 136.09 (s), 139.79 (d, $^4J_{PC}$ = 4.02 Hz), 142.43 (s) 176.30 (d, $^2J_{PC}$ = 8.60 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 21.03.

trans-N-[1-Oxo-3-(2′-pyridyl)propen-2-yl]-triphenylphosphinimine **10f.** This compound was obtained as a pale yellow powder. Mp 156°C. IR (KBr), 3040, 3020, 2980, 1630, 1580, 1550, 1540, 1480, 1460, 1340, 1250, 1080, 1010, 980, 895, 830, 780, 740, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.81 (d, ^1J = 15.77 Hz, 1H, CH=), 7.61 (d, ^1J = 15.77 Hz, 1H, CH=) 7.2 (m, 2H, pyridine), 7.3–7.9 (m, 16H, aromatics), 8.61 (d, ^1J = 4.69 Hz, 1H, pyridine); ^{13}C NMR ($CDCl_3$), δ = 122.84 (s), 128.12 (d, $^1J_{PCi}$ = 99.63 Hz), 128.76 (d, $^2J_{PCo}$ = 12.07 Hz), 131.51 (s), 132.62 (d, $^4J_{PC}$ = 2.51 Hz), 132.82 (s), 133.17 (d, $^3J_{PCm}$ = 9.86 Hz), 135.15 (s), 139.27 (d, $^4J_{PC}$ = 10.92 Hz), 149.77 (s), 155.09 (s), 176.98 (d, $^2J_{PC}$ = 8.25 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 21.40.

trans-N-[1-Oxo-3-(2′-furanyl)propen-2-yl]-triphenylphosphinimine **10g.** This compound was obtained as a pale yellow powder. Mp 140°C. IR (KBr), 3060, 1640, 1480, 1430, 1330, 1235, 1110, 880 cm^1; ^1H NMR ($CDCl_3$) δ = 6.45 (dd, ^1J = 16.31 Hz, ^2J = 3.31 Hz, 1H, CH=), 6.74 (dd, ^1J = 16.31 Hz, ^2J = 3.06 Hz, 1H, CH=), 7.25–7.9 (m, 18H, aromatics); ^{13}C NMR ($CDCl_3$) δ = 112.26 (s), 113.56 (s), 119.56 (s), 128.16 (d, $^1J_{PCi}$ = 99.14 Hz), 128.81 (d, $^2J_{PCo}$ = 12.20 Hz), 132.2 (d, $^4J_{PCp}$ = 2.66 Hz), 133.04 (d, $^3J_{PCm}$ = 9.91 Hz), 144.63 (s), 150.87 (s), 176.34 (d, $^2J_{PC}$ = 8.35 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 21.20. Anal. calcd for $C_{25}H_{20}NO_2P$: C, 75.54; H, 5.08; N, 3.53; found: C, 75.55; H, 5.05; N, 3.55.

trans-N-[1-Oxo-3-(2′-thiophenyl)propen-2-yl]-triphenylphosphinimine **10h.** This compound was obtained as a pale yellow powder. Mp 118°C. IR (KBr), 3160, 3100, 1680, 1630, 1600, 1530, 1480, 1415, 1380, 1330, 1290, 1260, 1160, 1030, 930, 900, 800, 760, 560 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.71 (dd, ^1J = 15.56 Hz, ^2J = 2.73 Hz, 1H, CH=), 6.99 (dd, ^1J = 4.98 Hz, ^2J = 3.58 Hz, 1H, CH=), 7.22 (dd, ^1J = 15.33 Hz, ^2J = 4.04 Hz, 1H, CH=), 7.5–7.95 (m, 17H, aromatics); ^{13}C NMR ($CDCl_3$) δ = 126.41 (s), 127.27 (s), 127.64 (s), 127.73 (s), 128.16 (d, $^1J_{PCi}$ = 99.13 Hz), 128.8 (d, $^2J_{PCo}$ = 12.22 Hz), 132.2 (d, $^4J_{PCp}$ = 2.66 Hz), 132.4 (d, $^4J_{PC}$ = 4.17 Hz), 133.04 (d, $^3J_{PCm}$ = 9.91 Hz), 141.35 (s), 176.1 (d, $^2J_{PC}$ = 8.40 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 21.64. Anal. calcd for $C_{25}H_{20}NOPS$, C, 72.62; H, 4.88; N, 3.39; S, 7.75; found: C, 72.50; H, 4.89; N, 3.41; S, 7.78; FAB^+(70eV) m/z; found, $M+H^{]+}$ = 414, calcd for $C_{25}H_{20}NPOS$: M, 413.47.

trans-N-[1-Oxo-3-(ethoxycarbonyl)penten-2-yl]-triphenylphosphinimine **12.** This compound was obtained as a pale yellow powder. Mp 104°C. IR (KBr), 3060, 2980, 1720, 1710, 1630, 1580, 1480, 1430, 1340, 1270, 1110, 980, 870, 720, 640, 530 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.35 (t, ^1J = 7.19 Hz, 1H, CH_3), 4.21 (q, ^1J = 7.20 Hz, 2H, CH_2), 6.81 (d, ^1J = 15.61 Hz, 1H, CH=), 7.21 (d, ^1J = 15.61 Hz, 1H, CH=), 7.5–7.9 (m, 15H, aromatics); ^{13}C NMR ($CDCl_3$) δ = 13.58 (s, CH_3), 29.70 (s, CH_2), 128.37 (d, $^1J_{PCi}$ = 99.13 Hz), 128.58 (d, $^2J_{PCo}$ = 12.58 Hz), 131.92 (d, $^4J_{PCp}$ = 2.51 Hz), 132.10 (d, $^3J_{PCm}$ = 9.81 Hz), 133.07 (s), 139.59 (s), 171.41 (s, CO), 176.3 (d, $^2J_{PC}$ = 8.55 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 20.90.

N-N′-[1,4-Fumaroyl]bis-triphenylphosphinimine **13.** This compound was obtained as a pale yellow powder. Mp 195°C. IR (KBr), 1630, 1610, 1530, 1480, 1370, 1230, 1160, 1070, 1050, 890, 830, 800, 770, 740, 580, 570 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.2 (m, $^3J_{HH}$ = 13.3 Hz, $^4J_{PH}$ = 4.8 Hz, 1H, CH=), 7.3–7.9 (m, 15H, aromatics), ^{13}C NMR ($CDCl_3$) δ = 127.65 (d, $^1J_{Pci}$ = 90.53 Hz), 128.59 (d, $^2J_{PCo}$ = 12.37 Hz), 132.7 (d, $^4J_{PCp}$ = 2.31 Hz), 133.25 (d, $^3J_{PCm}$ = 10.01 Hz), 138.50 (d, $^3J_{PC}$ = 21.13 Hz), 177 (d, $^2J_{PC}$ = 8.15 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 19.67; FAB^+(70eV) m/z; found, $M+H^{]+}$ = 635, calcd for $C_{40}H_{32}N_2P_2O_2$: M, 634.

N-[2-(Ethoxycarbonyl)benzoyl]-triphenylphosphinimine **15.** This compound was obtained as a pale yellow powder. Mp 138°C. IR (KBr); 3150, 3060, 3020, 1750, 1650, 1640, 1610, 1530, 1510, 1480, 1370, 1290, 1210, 1170, 980, 870, 795, 740, 570 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.2 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 4.12 (q, $^3J_{HH}$ = 7 Hz, 2H, CH_2), 7.4–8 (m, 19H, aromatics); ^{13}C NMR ($CDCl_3$) δ = 13.90 (s, CH_3), 60.98 (s, CH_2) 127.51 (s), 128.19 (d, $^1J_{Pci}$ = 99.13 Hz), 128.61 (d, $^2J_{PCo}$ = 12.73 Hz), 129.03 (s), 129.49 (s), 129.68 (s), 132.30 (d, $^4J_{PCp}$ = 2.91 Hz), 133.2 (d, $^3J_{PCm}$ = 10.06 Hz), 133.9 (s), 139.1 (s), 171.20 (s, CO), 176.3 (d, $^2J_{PC}$ = 8.55 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 21.70.

N-N′-[Phthaloyl]bis-triphenylphosphinimine **16.** This compound was obtained as a pale yellow powder. Mp 229°C. IR (KBr), 3060, 3020, 1645, 1630,

1610, 1530, 1480, 1380, 1160, 790, 770, 740, 580, 565 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.2–7.8 (m, 34H, aromatics); ^{13}C NMR ($CDCl_3$) δ = 128.04 (s), 128.37 (d, $^2J_{Pco}$ = 12.07 Hz), 128.44 (d, $^1J_{Pci}$ = 98.93 Hz), 131.90 (d, $^4J_{PCp}$ = 2.76 Hz), 132.19 (s), 133.30 (d, $^3J_{PCm}$ = 10.01 Hz), 140.90 (d, $^3J_{PC}$ = 20.83 Hz), 179.8 (d, $^2J_{PC}$ = 8.60 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 18.38.

N-[(2-Cyano) benzoyl]triphenylphosphinimine **23b.** This compound was obtained as a pale yellow powder. Mp 152–155°C. IR (KBr), 3055, 2960, 2880, 2220, 1600, 1580, 1555, 1430, 1330, 1260, 1100, 1030, 930, 800, 720, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.45 (m, 8H, aromatics), 7.65 (d, ^1J = 3.85 Hz, 2H, aromatics), 7.85 (m, 7H, aromatics), 8.2 (d, ^1J = 3.77 Hz, 2H, aromatics); ^{13}C NMR ($CDCl_3$) δ = 113.04 (s), 119.81 (s, CN), 127.51 (d, $^1J_{PCi}$ = 99.58 Hz), 128.73 (d, $^2J_{Pco}$ = 12.42 Hz), 130.01 (s), 130.65 (d, $^4J_{PCp}$ = 2.56 Hz), 131.7 (s), 132.24 (d, $^3J_{PC}$ = 2.66 Hz), 133.3 (d, $^3J_{PCm}$ = 10.21 Hz), 134.26 (s), 142.1 (s), 175.2 (d, $^2J_{PC}$ = 8.55 Hz, CO); ^{31}P NMR ($CDCl_3$) δ = 22.63.

REFERENCES

[1] H. Staudinger, E. Hauser, *Helv. Chem. Acta, 4,* 1921, 861.

[2] W. Wiegräbe, H. Bock, *Chem. Ber., 100,* 1967, 1120.

[3] S. Bittner, Y. Assaf, P. Krief, M. Pomerantz, B. T. Ziemnicka, C. G. Smith, *J. Org. Chem., 50,* 1985, 1712.

[4] V. I. Shevchenko, A. S. Shtepanek, A. V. Kirsanov, *Zh. Obshch. Khim., 32,* 1962, 2595.

[5] M. Biddlestone, R. A. Shaw, *J. Chem. Soc. Dalton Trans.,* 1975, 2527.

[6] H. R. Kricheldorf, *Synthesis,* 1972, 695.

[7] K. Yamada, N. Inamoto, *Bull. Chem. Soc. Jap., 45,* 1972, 1559.

[8] H.-J. Cristau, J. Kadoura, E. Torreilles, *Bull. Soc. Chim. Fr.,* 1989, 515.

[9] H.-J. Cristau, E. Manginot, E. Torreilles, *Synthesis,* 1991, 382.

[10] H. R. Gamrath, U.S. Patent, 2,764,609, 1956; *Chem. Abstr., 51,* 1957, 5823h.

[11] J. Dunogues, P. Rabin, B. Clin, *Bull. Soc. Chim. Fr.,* 1987, 997.

[12] J. Bruson, *J. Am. Chem. Soc., 64,* 1942, 2457.

[13] D. Barnard, L. Batemen, *J. Chem. Soc.,* 1950, 926.

[14] N. A. Bumagin, N. P. Andryukhova, *Dokl. Chem. (Engl. Transl.), 313,* 1990, 183.

[15] V. Auwers, *Chem. Ber., 66,* 1933, 1198.

[16] M. Strell, E. Kopp, *Chem. Ber., 91,* 1958, 1621.

[17] R. Reitz, *Chem. Ber., 89,* 1956, 2570.

[18] J. W. Macfraland, L. H. Conover, H. L. Howes, *J. Med. Chem., 12,* 1969, 1066.

[19] C. K. Saures, R. J. Cotter, *J. Org. Chem., 26,* 1961, 6.