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ONE POT SYNTHESIS OF 2-VINYL-1-AZADIENES AND DIVINYLKETONES.

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SUMMARY: Preparation of 2-vinyl-1-azadienes and 1,4-pentadien-3-ones from *N*-phenyl-triphenyl-λ^5-phospazene, triphenyl(prop-2-ynyl)phosphonium bromide and aldehydes is described.

Divinylketones represent synthetically attractive building blocks for cyclopentanoid natural products[1], through the Nazarov reaction [2]. They have been extensively used not only as dienophiles in the Diels-Alder reaction [3], but also in the Robinson annellation[4]. On the other hand, 1-azadienes are very versatile starting materials in the development of a wide variety of methods for the construction of β -antibiotics [5] and six membered heterocycles [6].

Previously, several procedures of synthesis of divinyl ketones have been reported [7,8], however the preparation of such compounds is far from simple [8]. Moreover the preparation of the $\alpha-\beta-$unsaturated imines from amines and carbonyl compounds, specially in the case of ketones, only yields good results in very specific cases [9] and it generally leads to Michael addition [10].

In this context we have recently studied the [2+2] cycloaddition reaction of acetylene acid esters with phosphonium ylides and the related isoelectronic λ^5-phospazenes [11] as well as their ability as starting materials in the preparation of 2-aza-1,3-dienes [12] and phosphorilated β-enamines [13]. Continuing our interest in the use of λ^5-phosphazenes as intermediates in organic synthesis, we describe a very easy one- pot preparation of 2-vinyl-1-aza-1,3-dienes and 1,4-pentadien-3-ones from comercially available starting reagents [14], as *N*-phenyl-*P*,*P*,*P*-λ^5-phosphazenes **1**, propargyltriphenylphosphonium bromide **2** and aldehydes.

Thus, triphenyl(prop-2-ynyl)phosphonium bromide **2** reacts with λ^5-phosphazenes [15] **1** at room temperature for 36-40 h leading to the phosphonium ylide **3**, in a similar way to that described for other acetylenic compounds [11]. Subsequent treatment of **3**, without its isolation, with aldehydes (1-24 h, see table) affords the corresponding β-enamino phosphonium salts [16] **4** in excellent yields. Compounds **4** were characterized on the basis of their spectroscopic data [17]. For instance, the enaminic -CH of **4a** give a ^{1}H resonance at δ=4.85 ppm ($^2J_{PH}$= 14.1 Hz) and a ^{13}C resonance at δ=61.4 ppm($^1J_{PC}$=117.9 Hz) as well resolved doublets, while the vicinal coupling constant ($^3J_{HH}$= 15.8 Hz) between the vinylic protons reveals the *E* configuration .

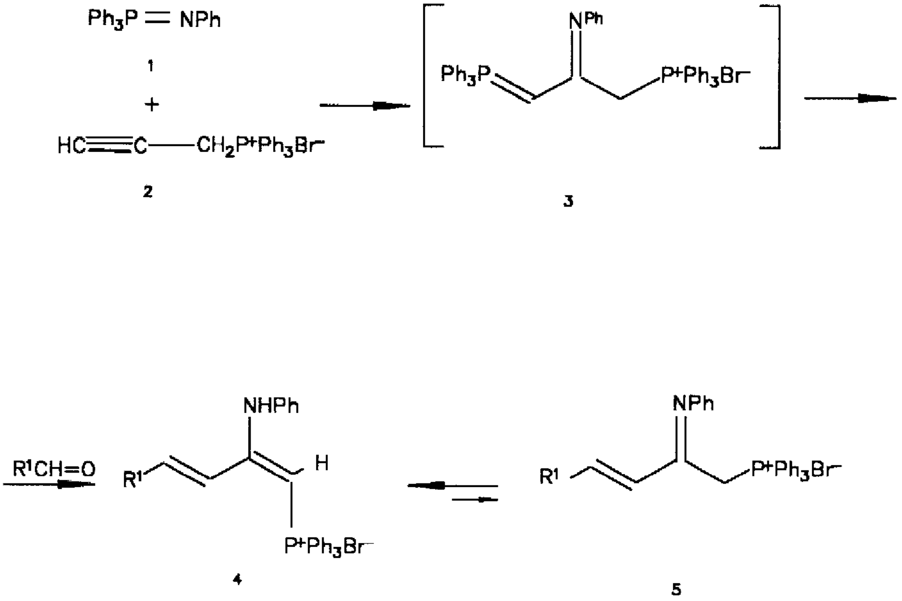


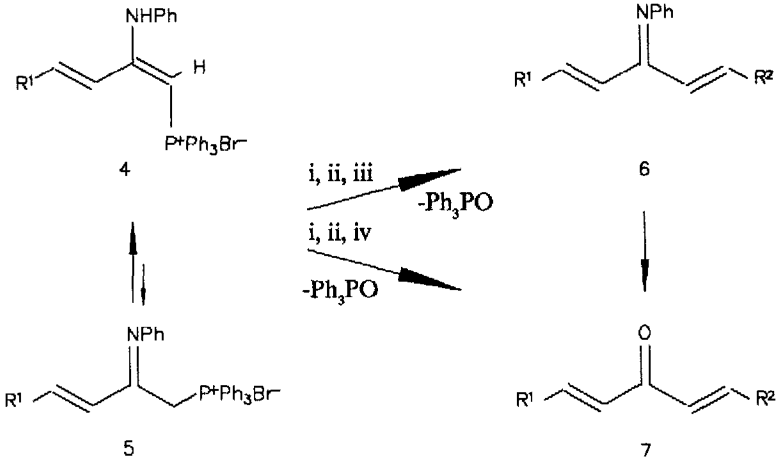
Table of phosphonium salts **4**

Compound	R^1	Reaction Time(h)[a]	Solvent	T(°C)	m.p.(°C)[b]	Yield (%)
4a	C_6H_5	14	CH_2Cl_2	25	157-158(d)	93
4b	*p*-$CH_3.C_6H_4$	16	CH_3CN	60	69-70(d)	86
4c	*o*-$NO_2C_6H_4$	10	CH_2Cl_2	25	191-193(d)	88
4d	2-Furyl	20	CH_3CN	60	210-212(d)	79
4e	H	1	CH_2Cl_2	25	217-218(d)	95
4f	CH_3CH_2	24	CH_2Cl_2	40	146-147(d)	68

[a] Addition of aldehydes to the crude reaction mixture from **1** and **2**

[b] From ethylacetate-CH_2Cl_2

Metallation of compounds **4** with butyllithium followed by addition of aldehydes and aqueous work-up leads to 2-vinyl-1-aza-1,3-dienes **6**[18], isolated by means of a short chromatography columm with ether as eluent. This result parallels that reported for the C-alkylation of β-enamino λ^5-phosphazenes[13]. Acid hydrolysis of compounds **6** with 2N H_2SO_4 affords the corresponding divinyl ketones **7**[19]. These derivatives **7** can be also prepared from phosphonium salts **4** and aldehydes when the reaction was quenched with 2N H_2SO_4.



i: BuLi, -70°C; ii: $R^2CH=O$, -70°C to 25°C, THF; iii: H_2O; iv: H_3O^+

It is noteworthy that the preparation of divinylic ketimines **6** and ketones **7** does not require the isolation and purification of the phosphonium salts **4**. Improved overall yields are obtained in one pot reaction when these salts **4**, after evaporation of the solvent, are directly metallated in THF with subsequent addition of aldehydes and aqueous or acid work-up, respectively.

Table of 2-vinyl-1-aza-1,3-dienes 6 and 1,4-pentadien-3-ones 7 prepared

Compound	R^1	R^2	m.p.(°C)[a]	Yield(%)[b]
6a	C_6H_5	C_6H_5	97-98	86(84)
6b	o-$NO_2C_6H_4$	C_6H_5	109-110	84(81)
6c	C_6H_5	$C_6H_5CH=CH$	oil($R_F=0.8$)[c]	78(75)
6d	2-Furyl	$C_6H_5CH=CH$	oil($R_F=0.9$)[c]	72(70)
6e	H	C_6H_5	oil($R_F=0.7$)[c]	85(82)
7a	C_6H_5	C_6H_5	105-106	88(82)
7b	o-$NO_2C_6H_4$	C_6H_5	92-93	84(79)
7c	C_6H_5	$C_6H_5CH=CH$	oil($R_F= 0.8$)[c]	79(75)
7d	2-Furyl	$C_6H_5CH=CH$	oil($R_F=0.9$)[c]	74(71)

[a] From hexane

[b] Yields from phosphonium salts **4**. Yields given in parenthesis refer to the one-pot process from **1** and **2**

[c] Silica gel, ether

REFERENCES

1.- B.M. Trost, *Chem. Soc. Rev.* **1982,** *11*, 141. L.A. Paquette, *Top. Curr. Chem.* **1984,** *1*, 119. M. Ramiah, *Synthesis*, **1984**, 529.

2.- N.I. Nazarov, I.I. Zaretskaya, *Zh. Obshch. Khun*, **1957**, *27*, 693. G. Ohloff, K.H.Schulte, E. Demole, *Helv. Chim. Acta*, **1971**, *54*, 2913.

3.- G. Desimoni, G. Tacconi, *Chem. Rev.*, **1975**, *75*, 651. G. Desimoni, G. Tacconi, A. Barco, C.P. Pollini in "Natural Products Synthesis through Pericyclic Reactions". *Am. Chem. Soc.*, Washintong 1983. E. Ciganek, *Org. React.*, **1984**, *32*, 1.

4.- M.E. Yung, *Tetrahedron*, **1976**, *32*, 3. R.E. Gawley, *Synthesis*, **1976**,.777.

5.- D.A. Evans, J.M. Williams, *Tetrahedron Lett.*, **1988**, *29*, 5065. J. Lasarte, C. Palomo, J.P. Picard, J. Dunogues, J.M. Aizpurua, *J. Chem. Soc. Chem. Comm.*, **1989**, 72.

6.- D.L. Boyer, S.M. Weinreb in "Hetero Diels-Alder Methodology in Organic Synthesis", Academic Press, San Diego, 1987, p. 239.

7.- J. Barluenga, F. Aznar, M.P.Cabal, C.Valdés, *Tetrahedron Lett.*, **1989**, *30*, 1413.

8.- M.R. Peel, C.R. Johnson, *Tetrahedron Lett.*, **1986**, *27*, 5947 and references therein cited.

9.- S.K. Malholra, D.F. Hookley, F. Johnson, *J. Am. Chem. Soc.*, **1967**, *89*, 2794.

10.- M. S. Gibson in "The Chemistry of Amino Group", Ed. S. Patai, J. Willey, London,1968, p. 63.

11.- J. Barluenga, F. López, F. Palacios, *J. Chem. Soc. Chem. Comm.*, **1986**, 1574. J. Barluenga, F. López, F. Palacios, F. Sánchez, *Tetrahedron Lett*, **1988**, *29*, 381.

12.- J. Barluenga, M. Ferrero, F. Palacios, *Tetrahedron Lett*, **1988**, *29*, 4863.

13.- J. Barluenga, F. López, F. Palacios, F.H. Cano, M. C. Foces, *J. Chem. Soc. Perkin TransJ*, **1988**, 2329.

14.- Reagents **1** and **2** are available from Aldrich.

15.- E.E. Schweiser, C.S. Kim, C.S. Labau, W.P. Murray, *J. Chem. Soc. Chem. Comm.*, **1973**, 7.

16.- Due to the imine-enamine equilibrium, crude compounds **4** contain a small proportion of the iminic tautomer **5** (10-19%); the tautomers ratio was determinated by ^{31}P-NMR ($\delta = 16.5$ ppm for **4a** and $\delta = 24.1$ ppm for **5a**, 83:17).

17.- Spectral data for **4a**: δ_H(300 MHz, $CDCl_3$): 4.85(d,1H,$^2J_{PH} = 14.1$,CH=), 6.1(d,1H $^3J_{HH} = 15.8$, CH=), 6.8-7.85(m,ArH), 8.0(d,1H, $^3J_{HH} = 15.8$,CH=), 10.4(s, 1H,NH); δ_C (75 MHz, $CDCl_3$): 61.4(d, $^1J_{PC} = 117.9$,C-1), 119.7(d,$^3J_{PC} = 7.0$,C-3), 122.6-148.3(CArom + C-4), 161.0(d,$^2J_{PC} = 11.6$,C-2); δ_P (120 MHz, $CDCl_3$): 16.5 ppm. MS (70 ev): m/z=481 (M^+-HBr).

18.- Spectral data for **6a**: δ_H(300 MHz, $CDCl_3$): 6.76(d,1H, $^3J_{HH} = 16.5$,CH=), 6.91-7.6(m,ArH + CH=), 7.58(d,1H, $^3J_{HH} = 16.5$,CH=); δ_C (75 MHz, $CDCl_3$): 120.8-150.7(CArom + CH=),162.8(C-3) ppm; MS(70 ev): m/z=309 (M^+).

19.- Spectral data for **7a**: δ_H(300 MHz, $CDCl_3$): 7.12(d,1H,$^3J_{HH} = 15.8$,CH=), 7.25-7.60(m,ArH), 7.64(d,1H,$^3J_{HH} = 15.8$,CH=); δ_C (75 MHz, $CDCl_3$): (CArom + C-2 + C-4), 143(C-1 + C-5), 188(C-3) ppm; MS(70 ev)m/z=234 (M^+).

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