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A GENERAL ONE-POT SYNTHESIS OF 1,3-BUTADIENYL PHOSPHANES

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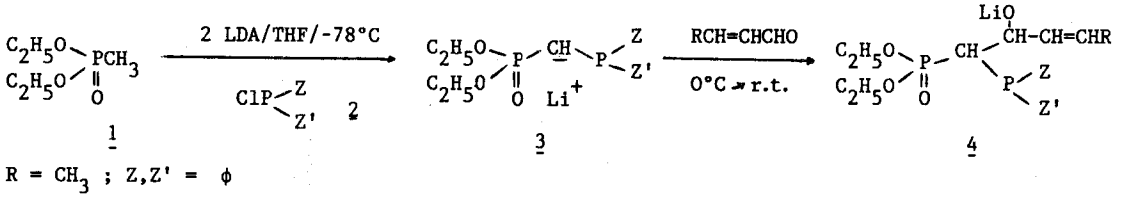
Abstract: The condensation of a six membered cyclic phosphonyl-phosphanyl anion with an α, β-unsaturated aldehyde leads to the direct generation of a 1,3-butadienyl phosphane according to a Wittig-Horner type elimination.

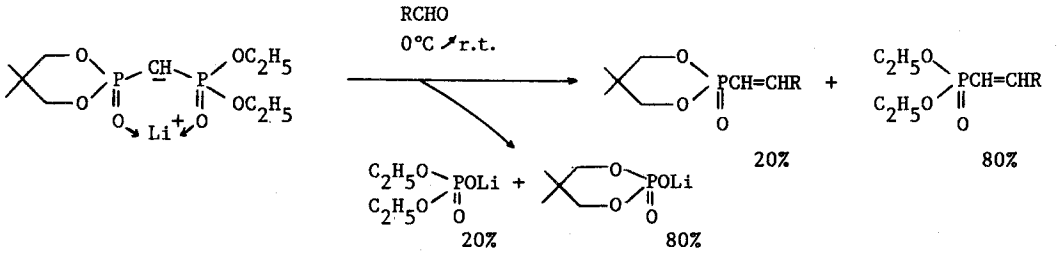
The 1,3-butadienyl phosphanes $Z_2P(CH=CH)_2R$ (Z=R,RO,NR2) are compounds of particular interest in the field of coordination chemistry because they represent the fusion between two very popular ligands: a tricoordinated phosphorus and a conjugated diene[1]. However the potential they afford for building complexes has been largely unexplored due to the difficulties to prepare such unsaturated phosphorus structures[2]. As far as we know the first synthetic approach reported in 1980[3] consists in the reduction/complexation of a parent phosphine sulfide and is a five-step process. More recently it has been proposed a different strategy which is a transfer reaction from zirconium dienyls to phosphorus[4] but though the process is shorter (two-step) it requires a quite sophisticated starting material (enyne).
In this communication, we present a new and more facile access to the title compounds which is based on a Wittig-Horner type reaction. We previously described a performing one-pot preparation of α, β-unsaturated tetracoordinated phosphorus species $Z_2P(O)CH=CHR$ where the direct generation of a methylene diphosphonic anion was involved[5]. Analogously it was attractive to generate unsymmetrical methylene anions i.e. bearing two phosphorus atoms in different coordination number (P^{III}/P^{IV})(3 Scheme I) and react them with α,β-unsaturated aldehydes in order to built butadienyl phosphanes systems. Unfortunately though the phosphonyl-phosphanyl entity 3 is easily obtained by condensation of diethyl methylphosphonate 1 on a chlorophosphane 2 in presence of 2 eq. of LDA, the further addition of a carbonyl reagent RCH=CHCHO doesn't induce the Wittig-Horner elimination. The reaction stopped at the formation of the aldol adduct 4 which exhibits a great resistance to decomposition into conjugated olefin (after 3h at + 60°C 4 is recovered unchanged). 3 and 4 have been characterized in situ by ^{31}P NMR [δ ($CDCl_3$) ppm : (3, +43, -21, AB system ; ^2JPP (Hz)=+156) (4 ; +24.7, -29.7 ; AB system ; ^2JPP(Hz)=+43.9].



R = CH_3 ; Z,Z' = φ

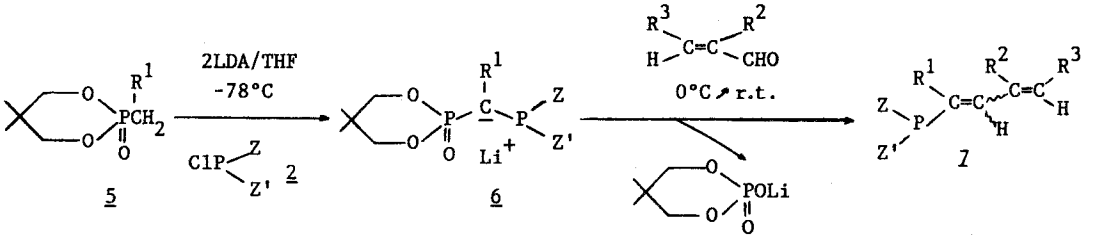
- Scheme I -

According to the mechanism proposed in the literature[6], the decomposition of 4 should be induced by the intramolecular nucleophilic attack at phosphorus (P^{IV}) leading to a transient pentacoordinated cyclic intermediate (oxaphosphetane P^V) rapidly cracked into salt and olefin (syn elimination). As known the nucleophilic attacks at tetracoordinated phosphorus are very sensitive to substituent effects, and specially cyclic substrates (five or six-membered phosphates, phosphinates, phosphonates) have shown enhanced reactivities compare to open chain analogues[7]. Furthermore during our investigations on the bisphosphonic species, we remarked the greater mobility of the six-membered ring group 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane with regard to its diethyl phosphonyl equivalent. In fact when a competitive elimination is run between these two phosphonyl groups the cyclic phosphate salt is preponderantly eliminated (Scheme II).



- Scheme II -

These observations brought us to use cyclic phosphonates as starting materials in order to favor the decomposition of the corresponding aldol adducts. Thus 5,5-dimethyl-2-oxo-2-alkyl-1, 3,2-dioxaphosphorinanes 5 which are stable solids easily accessible[8] have been tested in the reaction (Scheme III).



- Scheme III -

According to Scheme III, the addition of an α,β-unsaturated aldehyde on the in situ generated anion 6 leads after return to room temperature to the spontaneous formation of the desired 1,3-butadienyl phosphane 7. The condensation is usually run at 0°C excepted when R^1=Cl : a lower temperature is then required (-40°C) due to the unstability of the anion 6 when it is α-chlorinated, in other cases (R^1=H, CH_3) 6 is stable a few hours at room temperature. After removal of the salts, 7 is obtained in satisfactory yield and purity.

In sharp contrast to Scheme I, the intermediate aldol adduct is quite never detected what evidences the destabilizing effect of the ring.

In an attempt to explain this activation, we suggest that there are two factors involved :

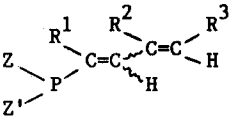
- a facilitated access to the phosphorus atom favoring the intramolecular cyclisation. The O-P-O angle values being similar in a six-membered ring and in an acyclic phosphonate (≃ 105°C)[9], the rigidity of the chair conformation and the resulting inhibition to rotation might be better implicated[10] -a contribution of the ring to an enhanced stability of the intermediate oxaphosphetane P^V resulting in an enhanced rate of the nucleophilic attack[11]. However more research will be required to fully understand this substituent effect.

The various compounds summarized in table I tend to prove the generality of the method. The large range of substituents available on phosphorus and on the diene moiety will permitt to modulate the interaction of these two coordinating sites with a metal. Equally the structures containing P-N bonds (entries 9 12) easily convertible into P-Cl or P-H bonds[12] are of particular interest for further synthetic transformations.

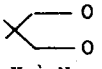
In every case the preferential configuration of the newly formed double bond is that bearing the P atom and the existing double bond in trans (E when R^1 = H, CH_3 ; Z when R^1 = Cl). The obtention of only one isomer when R^1 = H (entries 1-3 , 7-10) and of a mixture when $R^1 \neq H$ (entries 4,5,11) is typical of Wittig-Horner reactions where the stereochemistry may vary with the steric hindrance of the anion[13]. The bulkiness of the reactants constitute also a limitant factor for the reactivity : when simultaneously R^1, R^2, R^3 are alkyl groups (entry 6), the intermediate aldol adduct is again detectable and shows a sluggish and partial decomposition into 7.

Work is actually in progress to overcome this steric limitation and to investigate more deeply the stereocontrol of the reaction.

TABLE I : 1,3-BUTADIENYL PHOSPHANES :



7

entry	Z	Z'	R^1	R^2	R^3	Yield [a] %	NMR ^{31}P ($CDCl_3$) δ ppm	^3JPH (Hz)	Configuration [b] of the new double bound
1	Φ	Φ	H	H	CH_3	80	-15.1	10.1	E
2	Φ	Φ	H	Br	Φ	70	-14.7	10.9	E
3	Φ	Φ	H	CH_3	C_2H_5	55	-14.5	15.4	E
4	Φ	Φ	Cl	H	CH_3	64	+8.3 -8.1	10.2 31.5	Z 70 [c] E 30
5	Φ	Φ	CH_3	H	CH_3	50	+4.1 -17.1	13.6 -	E 90 [c] Z 10
6	Φ	Φ	CH_3	CH_3	CH_3	incomplete reaction			
7	C_2H_5O	C_2H_5O	H	H	CH_3	35	+159.0	15.5	E
8			H	CH_3	H	85	+145.0	13.6	E
9	$(C_2H_5)_2N$	Φ	H	H	CH_3	68	+53.0	10.7	E
10	$(C_2H_5)_2N$	Φ	H	CH_3	C_2H_5	54	+56.7	15.3	E
11	$(C_2H_5)_2N$	Φ	Cl	H	CH_3	54	+64.6 +50.4	10.2 -	Z 80 [c] E 20

a-Most of the compounds were isolated as clear or pale yellow oils excepted for entry 2 a brown solid has been obtained. All of them have been characterized by ^1H and ^{13}C NMR elemental analysis and/or mass spectrometry. b- The geometry of the double bond α to the phosphorus atom has been determined by ^1H NMR (Brüker AC 200) and ^1H { ^{31}P } NMR (Brüker WP 80) and according to spectroscopic data of vinyl phosphanes available in the literature[14] . c- The ratio E/Z has been measured by integration of ^{31}P NMR signals.The ^3JPH (trans) was not measurable for entries 5, 11 .

In conclusion, the availability of starting materials, the mild reaction conditions and the generality towards several different structures make the present method a very convenient route to 1,3-butadienyl phosphanes.

This study has been focused on butadienyl skeletons but the preparation of less or more unsaturated systems $Z_2P(CR{=}CH)_nR$ (n = 1, n>2) is currently under investigation.

General procedure : to a stirred solution of lithium diisopropyl amide (40 mmol from 4.1g diisopropylamine and 27 ml of 1.6 M n-butyllithium in hexane, 2.0 eq) in anhydrous THF (30 ml) at -78°C is added a solution of 5 (20 mmol 1.0 eq) in anhydrous THF (20 ml) such that the temperature remained below -60°C. The resulting solution is cooled to -78°C, stirred at that temperature 10 min and then the chlorophosphane 2 (20 mmol, 1.0 eq) is added dropwise. The solution is allowed to warm to 0°C (-40°C entry 4), the aldehyde is added dropwise, the reactional mixture is then warmed to +20°C (+30°C entry 5) and stirred 20 min at this temperature. The resulting solution is concentrated under reduced pressure, the residual viscous solid is suspended in hexane (200 ml) or hexane/benzene (85/15) then stirred during two hours. After removal of the precipitated salts by filtration on celite® the filtrate is concentrated to give pure 7. The salts can also be eliminated by whashing with deoxygenated water (2x15 ml) in CH_2Cl_2 the organic layer being then dried on Na_2SO_4, but due to the sensibility of 7 (side polymerisation and oxydation are frequently observed) direct trituration in hexane is usually preferred. 7 must be stored in the cold under inert atmosphere.

entry 10: ^{1}H NMR δ($CDCl_3$)ppm: 0.9(t,3H,$\underline{CH_3}CH_2CH$=);1.0(t,6H,$\underline{CH_3}CH_2N$);1.75(s,3H,$\underline{CH_3}C$=);2.15(dq, 2H,$\underline{CH_2}CH$=);3.0(dq ,4H,$\underline{CH_2}N$);5.6(t,1H,$CH_2\underline{CH}$=);6.15(dd,1H,P$\underline{CH}$=,^{2}JPH=7.2Hz);6.64(dd,1H,PCH=$\underline{CH}$, ^{3}JPH=15.3Hz,^{3}JHH(trans)=17.1Hz;7.3(m,5H,C_6H_5). ^{13}C NMR δ($CDCl_3$)ppm : 12.3($\underline{CH_3}C$=);14.0 ($\underline{CH_3}CH_2C$=);15.1($\underline{CH_3}CH_2N$);21.9($\underline{CH_2}CH$=);44.4($\underline{CH_2}N$);125.2(PCH=$\underline{C}H$,^{2}JCP=14.2Hz);127.5(C_4,arom) ;128.2($C_{3,5}$,arom);130.6($C_{2,6}$,arom);133.8(Cq,arom,^{1}JCP=12Hz);137($C_2H_5\underline{C}H$=);142.5($CH_3\underline{C}$=);147.7(P$\underline{CH}$= (^{1}JCP=36Hz). mass spectrum (E.I., 70 ev): m/z 275(M,47%),246(M-C_2H_5,77%),176(100%).

References and Notes

1 . M. Cais and N. Maoz, J. Chem. Soc. A, 1971, 1811. M.A. Bennett, R.N. Johnson and I.B. Tomkins, J. Amer. Chem. Soc., 1974, 96, 61. W. Winter, Angew. Chem., Int. Ed. Engl., 1976, 15, 214.

2 . C.A. Aufdermarsch, Jr., J. Org. Chem., 1964, 29, 1994. D. Gloyna and H.G. Henning, Angew. Chem., Int. Ed. Engl., 1966, 5, 847. F. Mathey and G. Muller, Can. J. Chem., 1978, 56, 2486 and references cited herein.

3 . F. Mathey, F. Mercier and C. Santini, Inorg. Chem., 1980, 19, 1813.

4 . M.D. Fryzuk, G.S. Bates, C. Stone, J. Org. Chem., 1988, 53, 4425.

5 . E.E. Aboujaoude, S. Lietje, N. Collignon, M.P. Teulade and P. Savignac, Tet. Lett., 1985, 26, 4435. P. Savignac, M.P. Teulade, E.E. Aboujaoude and N. Collignon, Synt. Comm., 1987, 17, 1559.

6 . B. Deschamps, G. Lefebvre and J. Seyden-Penne, Tetrahedron, 1972, 28, 4209. J. Boutagy and R. Thomas, Chem. Rev., 1974, 74, 87. W.S. Wadsworth, Org. Reactions, 1978, 25, 73. E. Breuer S. Zbaida and E. Segall, Tet. Lett., 1979, 2203.

7 . J.R. Cox, Jr., and O.B. Ramsay, Chem. Rev., 1964, 64, 317. R.S. Edmundson and J.O.C. Wrigley Tetrahedron, 1967, 23, 283. R.D. Cook, C.E. Diebert, W. Schwarz, P.C. Turley and P. Haake, J. Amer. Chem. Soc., 1973, 95, 8066. E. Breuer and D.M. Bannet, Tetrahedron, 1978, 34, 997. S. Li, X. Liao and C. Yuan, J. Phys. Org. Chem., 1989, 2, 146.

8 . 5 are readily obtained by condensation of $R^1CH_2P(O)Cl_2$ and the 2,2-dimethyl-1,3-propanediol in CH_2Cl_2 according to M.P. Teulade, P. Savignac, E.E. Aboujaoude and N. Collignon, J. Organomet. Chem., 1986, 283. The 5,5-dimethyl series is used preferentially to the hydrogenated series because these phosphonates are solid compounds easy to purify and to handle ; otherwise the two methyl groups have no influence on the reactivity. For a recent review on the preparation of cyclic phosphonates see : C. Yuan,S. Li, Z. Cheng, Synthesis, 1988, 186.

9 . T.A. Beineke, J. Chem. Soc., Chem. Commun., 1966, 23, 861.

10. J.A. Mosbo and J.G. Verkade, J. Org. Chem., 1977, 42, 1549.

11. S.A. Bone, S. Trippett and P. Whittle, J. Chem. Soc. Perkin I, 1977, 80. P.M. Cullisard,A.D. Kaye, Tet. Lett., 1988, 29, 2081. S. Li, X. Liao and C. Yuan, J. Phys. Org. Chem., 1989, 2, 146.

12. M. Hofler and M. Schnitzler, Chem. Ber., 1972, 105, 1133. F. Mercier and F. Mathey, Tet. Lett., 1985, 1717.

13. T.H. Kinstle and B.Y. Mandanas, J. Chem. Soc., Chem. Commun., 1968, 1699. G. Etemad-Moghadam and J. Seyden-Penne, Tetrahedron, 1984, 40, 5153. Ibidem, Bull. Soc. Chem. Fr., 1985, n°3, 448.

14. S.O. Grim, R.P. Molenda and J.D. Mitchell, J. Org. Chem., 1980, 45, 250. M. Duncan and M.J. Gallagher, Org. Magnet. Res., 1981, 15, 37.

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