Tetrahedron Letters,Vol.27,No.23,pp 2635-2638,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A SIMPLE PREPARATION OF TERVALENT PHOSPHIRENES

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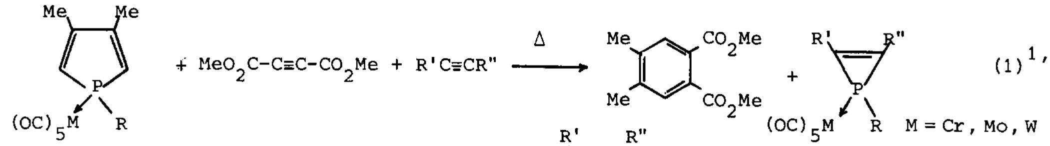
Summary : 1-Chlorophosphirenium salts obtained from $RPCl_2$, alkynes, and $AlCl_3$ are easily reduced by tributylphosphine around 0°C to give the corresponding tervalent phosphirenes ; when $RPCl_2$ is replaced by PCl_3, the same overall scheme gives a 1-(β-chlorovinyl)phosphirene which formally results from the addition of a second molecule of alkyne onto the P-Cl bond of the expected 1-chlorophosphirene.

Three syntheses of the phosphirene ring are available today [1-4]. All these methods



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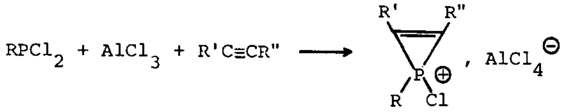

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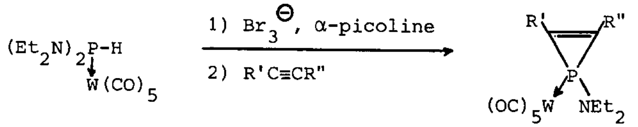
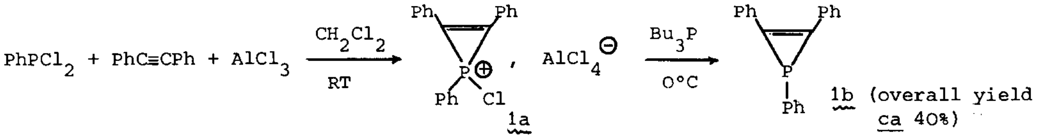


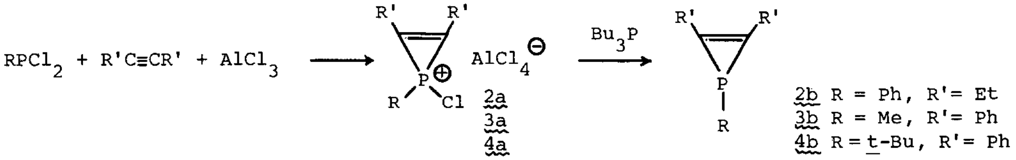
(3)[4]

formally involve the cycloaddition of an electrophilic phosphorus species $[R\text{-}P{=}M(CO)_5$, $R\text{-}\overset{\oplus}{P}\text{-}Cl$, or $Et_2N\text{-}P{=}W(CO)_5]$ onto a carbon-carbon triple bond. They just differ by the techniques which are used for generating such species. The first and last methods yield very stable complexes from which tervalent phosphirenes have been prepared for the first time by decomplexation[2,5]. While studying these very peculiar phosphines[2], we found that the reactivity of their lone pair at phosphorus is weak and that their quaternization is slow and difficult. This observation suggested that, conversely, the unstable chlorophosphirenium salts prepared according to eq 2 [3] might be easily reduced at low temperature thus avoiding the collapse of the ring. Accordingly, we attempted to reduce these salts in situ with tributylphosphine. The first experiments were performed with the $PhPCl_2$-Ph_2C_2 adduct. The reduction was successfully carried out around 0°C and gave the expected 1,2,3-triphenylphosphirene 1b (eq 4).



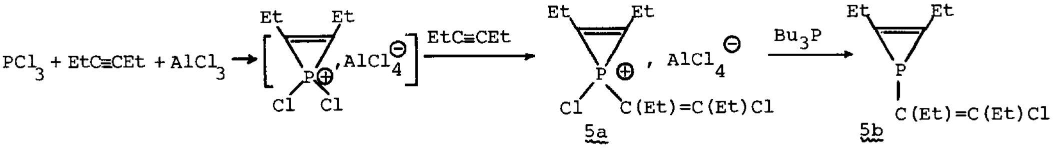
(4)

Using similar conditions, we also attempted to reduce a series of other adducts (eq 5).



(5)

The trisubstituted phosphirenes 2b-4b were characterized by ^{31}P NMR spectroscopy. Contrary to 1b, their stability appears to be rather low. Indeed, attempted purification by chromatography on silica gel caused decomposition. For example, 2b gave mainly 1,2,3-triphenyl-4,5-diethyl-1,2,3-triphospholene which was identified by its ^{31}P NMR spectrum (AB_2 system : δ_A -42.7 ppm, δ_B +43.6 ppm, $^1J(A-B)$ 242.5 Hz, see ref 6). This decomposition seems to be catalyzed by Lewis acids since adding a tertiary amine to the medium stabilizes 2b. In practice, 2b-4b were just extracted from their CH_2Cl_2 solution by hexane and kept around 0°C. At room temperature, they slowly decompose. The success of the reduction heavily depends on the nature of the R substituent at phosphorus. The reaction of Me_2N-PCl_2 or $i-Pr_2N-PCl_2$ with $AlCl_3$ and EtC≡CEt in CH_2Cl_2 apparently produces the expected cyclic adducts ($\delta^{31}P$ -61.1 and -76.6 ppm respectively) but these species do not react with Bu_3P under the standard conditions. Still a different behaviour was observed when replacing $RPCl_2$ by PCl_3. The expected adduct reacts with a second molecule of alkyne (eq 6).



(6)

The final phosphirene 5b was identified by ^{13}C and ^{31}P NMR spectroscopy and converted into its $P-W(CO)_5$ complex which was more completely characterized.

This new methodology for preparing tervalent phosphirenes is obviously the best one for obtaining simple compounds such as 1b. However, the two other methods (eqs 1 and 3) keep their usefulness for the synthesis of functional species at phosphorus (P-Cl[4,7], P-OR[8], $P-NR_2$[4], P-H[9], etc...) or at carbon[2].

Acknowledgements : Financial support from the Commission of the European Communities (Stimulation Action) is gratefully acknowledged (grant to S.L.).

Experimental Data

Synthesis of **1b**

A solution of tolan (2.00 g, 11.22 mmol) in 3 mL of CH_2Cl_2 was added within 1 min. to a solution of $PhPCl_2$ (1.50 mL, 11.05 mmol) and $AlCl_3$ (2.00 g, 15.00 mmol) in 10 mL of CH_2Cl_2 at room temperature under vigorous stirring. After 20 min., the black crude solution was transferred into a solution of Bu_3P (3.30 mL, 13.38 mmol) in 5 mL of CH_2Cl_2 at 0°C within 5 min. under stirring. The phosphirene **1b** was isolated after chromatography on silica gel with hexane-CH_2Cl_2 (80:20) and evaporation of the solvents as a blue colored product, which can be purified by crystallization from hexane. Yield : 1.36 g, 4.75 mmol (43%). The spectroscopic characterization of **1b** is described in ref. 5.

Synthesis of **5b** and its P-W$(CO)_5$ complex

To a solution of PCl_3 (0.87 mL, 10 mmol) in 10 mL of CH_2Cl_2, $AlCl_3$ (1.90 g, 14.25 mmol) at first and then hexyne (1.70 g, 20.77 mmol) were added within 1 min. at room temperature. After all $AlCl_3$ was dissolved, the solution was cooled to -75°C and Bu_3P (3.00 mL, 12.15 mmol) was added within 5 min. The solution was warmed to room temperature. The phosphirene **5b** was then extracted with 3 x 15 mL of hexane and the hexane solution was added to 10 mmol of $W(CO)_5$.THF in 200 mL of THF. After evaporation of the solvents, the residue was chromatographed with hexane. The phosphirene P-W$(CO)_5$ complex crystallizes from hexane at 0°C. Yield : 1.82 g, 3.28 mmol (32.8%). Mass spectrum (EI, 20eV, ^{184}W, ^{35}Cl) : m/e 554 (M, 33%), 414 (M-5CO, 56%), 412 (100%).

Spectral data NMR spectra : δ +ve for downfield shifts in all cases, references Me_4Si or H_3PO_4

- $\delta^{31}P$ (CH_2Cl_2) : **1a** -70.6 ; **1b** -189.8 ; **2a** -60.5 ; **2b** -188.4 ; **3a** -70.1 ; **3b** -191.6, ^2J(P-C-H) 5.5 Hz ; **4a** -49.8 ; **4b** -149.6, ^3J(P-C-C-H) 11.4 Hz ; **5a** -73.7 ; **5b** -181.7 ; (**5b**)W$(CO)_5$ -162.5, $^1J(^{31}P-^{183}W)$ 269.3 Hz
- **5b** ^{13}C NMR ($CDCl_3$) : δ 124.3 [d, ^1J(C-P) 47.6 Hz, ring C], 140.4 [d, J(C-P) 33 Hz, vinyl C], 141.5 [d, J(C-P) 75.7 Hz, vinyl C]
- (**5b**)W$(CO)_5$ ^{13}C NMR ($CDCl_3$) : δ 135.3 [d, ^1J(C-P) 13.4 Hz, ring C], 138.7 [d, J(C-P) 2.5 Hz, vinyl C], 143.2 [d, J(C-P) 19.5 Hz, vinyl C], 196.4 [d, ^2J(C-P) 8.6 Hz, cis CO], 198.2 [d, ^2J(C-P) 30.5 Hz, trans CO]

References

[1] A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, J. Am. Chem. Soc., **104**, 4484 (1982)

[2] A. Marinetti and F. Mathey, J. Am. Chem. Soc., **107**, 4700 (1985)

[3] K.S. Fongers, H. Hogeveen, and R.F. Kingma, Tetrahedron Lett., **24**, 643 (1983)

[4] F. Mercier and F. Mathey, Tetrahedron Lett., **27**, 1323 (1986)

[5] A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, J. Chem. Soc., Chem. Commun., 45 (1984)

[6] C. Charrier, J. Guilhem, and F. Mathey, J. Org. Chem., **46**, 3 (1981)

[7] B. Deschamps and F. Mathey, Tetrahedron Lett., **26**, 4595 (1985)

[8] J.M. Alcaraz, J. Svara, and F. Mathey, Nouveau J. Chim., in the press

[9] B. Deschamps and F. Mathey, to be published

(Received in France 10 April 1986)