Pergamon

Tetrahedron Letters, Vol. 35, No. 20, pp 3297-3300, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0533-4

Alkylation of Phosphine PH_3 Generated from Red Phosphorus

Delphine Semenzin, Guita Etemad-Moghadam*, Dominique Albouy and Max Koenig*

Laboratoire d'Activation Moléculaire Par l'Electricité, le Rayonnement et l'Energie Sonore (AMPERES)
Université Paul Sabatier - 118, route de Narbonne - Bât. II R1 - 31062 Toulouse cedex - FRANCE

Key Words : Red Phosphorus - Phosphine - Alkylation - Ultrasound.

Abstract: The generation of phosphine PH_3 by alkaline hydrolysis of red phosphorus is realized. The subsequent alkylation of PH_3 by terminal alkenes and alkynes in basic media leading to the corresponding aliphatic and vinylic phosphine derivatives can occur by two-steps or one-pot reaction by a Michael-like reaction mechanism.

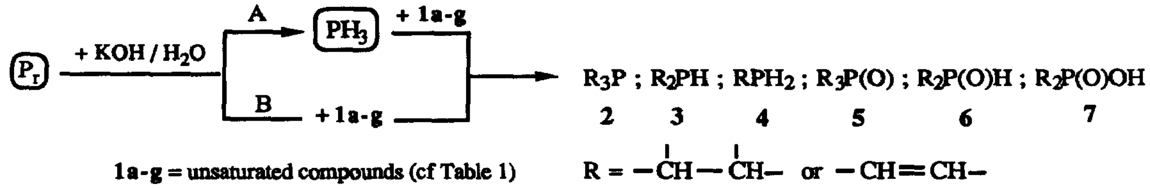
The generation of phosphine PH_3 by the alkaline disproportionation of white phosphorus, discovered by Gengembre at 1783,[1] is now used on an industrial scale so called Hoechst process.[2] In the laboratory scale, many other methods are described such as acidic hydrolysis of metal phosphides, alkaline hydrolysis of phosphonium halides, or thermal decomposition of the lower oxyacids of phosphorus.[3] They are few examples for the PH_3 generation from red phosphorus.[4] More surprising is the fact that in the recent literature or in industrial processes,[2-4] they are no reports on the observation of Schroetter in which the dissolution of amorphous red phosphorus in concentrated aqueous alkalies generates phosphine.[5] Here, we present the preparation of PH_3 by alkaline hydrolysis of red phosphorus and their subsequent alkylation by alkenes and alkynes in basic media, and the one-pot synthesis of phosphine derivatives from red phosphorus in basic media *via in situ* generated PH_3.

An aqueous concentrated KOH solution was added dropwise under stirring to red phosphorus.[6] After a short heating at 50 °C, this reaction becomes exothermic, and the released gas is trapped. By approach of a flame, this liberated gas ignites in air affording a dark-red precipitate of red phosphorus and a white vapour. If the oxidation-reduction reaction of white phosphorus in basic media could be transposed to red phosphorus, the released gas are a "PH_3 / H_2" mixture, according to two simultaneous reactions A and B:

$$4\ P_r + 3\ KOH + 3\ H_2O \longrightarrow PH_3 + 3\ KH_2PO_2 \qquad (A)$$

$$4\ P_r + 4\ KOH + 4\ H_2O \longrightarrow 2\ H_2 + 4\ KH_2PO_2 \qquad (B)$$

The liberated PH_3 is trapped in HMPA solution and the presence of phosphine is detected by the ^{31}P NMR spectra (δ ^{31}P = - 240, $^{1}J_{PH}$ = 186 Hz). In order to determine the quantitative value of released PH_3 from red phosphorus, among the various studied reactions of phosphine,[7-8] we have chosen its alkylation reaction by ethylenic and acetylenic compounds in the presence of strongly basic catalysts (scheme 1).



Scheme 1 - General scheme for the preparation of organophosphorus derivatives **2**-**7** from red phosphorus by two-steps reaction (pathway A) and one-pot reaction (pathway B).

For two-steps reaction (pathway A), as a typical experiment, the PH_3 generated from alkaline hydrolysis of red phosphorus in the first reactor, was bubbled in the second reactor containing a solution of acrylonitrile **1a** in acetonitrile / aqueous concentrated KOH at room temperature for 1 hour. The non-trapped gas is constituted only by H_2. The ^{31}P NMR spectra of the reaction mixture (reactor II) exhibit the presence of the tris-(2-cyanoethyl)-phosphine **2a** (70 %; δ ^{31}P = - 21.3, J_{PH} = 11 Hz), the bis-(2-cyanoethyl)-phosphine **3a** (15 %; δ ^{31}P = - 72, $^{1}J_{PH}$ = 195 Hz) and the tris-(2-cyanoethyl)-phosphine oxide **5a** (15 %; δ ^{31}P = 43.1) (Table 1). After extraction, **2a** is isolated in 45 % yield (calculated from the redox equation A). This generation of phosphine from alkaline hydrolysis of red phosphorus is a method so efficient as acid hydrolysis of zinc phosphide (Zn_3P_2).

We have then attempted the one-pot synthesis of organophosphines from red phosphorus under sonication at 20 kHz, since it is well known that the ultrasound is more effective in the case of heterogeneous solid-liquid reactions.[9-10] Furthermore, we have recently described that the sonication promotes the P-H addition on unsaturated compounds.[11] When a three-phase heterogeneous mixture of red phosphorus, concentrated aqueous solution of KOH, and acrylonitrile in acetonitrile is sonicated in a non-thermostated reactor at room temperature, the temperature rises after few minutes and the final temperature of the process reaches 70 °C after 10 minutes. For **1a**, the method B increases the percentage of phosphine oxide **5a** with respect to the method A. When DMSO is used as solvent instead of acetonitrile, **6a** is obtained predominantly. The method B improves substantially the rate of the reaction but for easily polymerisable unsaturated compounds such acrylonitrile or allyl alcool, it promotes also the formation of polymers as by-products.

However, the one-pot reaction becomes a suitable method for alkenes such as diphenylethylene **1d** or 4-vinylpyridine **1e**. The completion of the reaction requires 10 minutes of sonication for **1d** leading to a mixture of organophosphorus derivatives in 75 % overall yield of isolated products [**5d** (30 %; δ ^{31}P ($CDCl_3$) = 45.6, J_{PH} = 11 Hz), **6d** (10 %; δ ^{31}P ($CDCl_3$) = 27.2, J_{PH} = 5 Hz), and **7d** (35 %; δ ^{31}P (DMSO d_6) = 48.2, J_{PH} = 12.1 Hz)]. For **1e**, the tris-[2-(4-vinylpyridyl)-ethyl]-phosphine oxide **5e** (δ ^{31}P (CD_3OD) = 50.3, J_{PH} = 10 Hz) is obtained after 3 minutes of sonication in 40 % yield (isolated product). Nevertheless, the alkylation reaction of phosphine in basic media is not effective for non-terminal ethylenic compounds such as fumaronitrile **1b**, trans-stilbene **1c** or cyclohexene, whatever the used method (A or B). This is also the case for analogous acetylenic derivatives, e.g. 1-phenyl-1-propyne **1f**. However, with phenylacetylene **1g**, the one-pot reaction leads to the tris-

(Z-styryl)-phosphine **2g** (δ ^{31}P (C_6D_6) = - 60.5, $^3J_{PH}$ = 23 Hz) in 55 % yield (isolated product) for 10 minutes of sonication. It must be noted that in this case, the optimal conditions require the use DMSO as solvent and a catalytic amount of tributylphosphate (0.3 eq). Since the presence of P=O moiety appears necessary, a bubbling of oxygen through the mixture is realized in order to induce an autocatalytic formation of **2g**. No improvement is observed neither on the yield of phosphine **2g** nor on the amount of the phosphine oxide **5g**.

Table 1 - Alkylation of red phosphorus *via* phosphine PH_3 by ethylenic and acetylenic derivatives.

1		Method[a]	crude mixture (%)[b]	isolated product[c]	Yield (%)
a	NC—CH=CH$_2$	A	**2a** (70) **3a** (15) **5a** (15)	**2a**	45
		B	**2a** (30) **3a** (10) **5a** (60)		
b	NC—CH=CH—CN	A	no reaction		
		B	no reaction		
c	Ph—CH=CH—Ph	B	no reaction		
d	Ph$_2$C=CH$_2$	A	**3d** (traces)	**5d**	30
		B	**2d** (20) **3d** (60) **4d** (5) **6d** (15)	**6d** **7d**	10 35
e		B	**2e** (5) **3e** (5) **4e** (25) **5e** (65)	**5e**	40
f	Ph—C≡C—Me	B	no reaction		
g	Ph—C≡CH	A	**2g** (traces)	**2g**	55
		B	**2g** (90) **5g** (10)		

[a] Method A: two steps reaction; method B: one-pot reaction. For method B, DMSO is used as solvent except for **1a**.

[b] Percentage of the different organophosphorus derivatives in the reaction mixture, determined by ^{31}P NMR spectra [Potassium phosphinate (KH_2PO_2) does not take into account].

[c] Structures of all the isolated products are confirmed by elemental analyses and spectroscopic data.

Thus, for the easily oxidizable phosphine derivatives, the presence of P=O group in the products allows to avoid the use of the tri-butylphosphate, making easier the work-up. According to the redox-disproportionation of red phosphorus, the potassium phosphinate (δ ^{31}P = - 3, t, J_{PH} = 473 Hz) is always present as by-product in the "one-pot" reaction mixture. Altough phosphine is slightly acid, it is probable that in super-basic media, the reaction proceeds *via* a Michael-like mechanism. Thus, this new approach to the direct synthesis of organophosphorus compounds from the red phosphorus adds to the various methods recently described in this area.[12]

In conclusion, the generation of phosphine PH_3 by alkaline hydrolysis of red phosphorus is an attractive and efficient pathway requiring the cheap and safe raw materials. Its subsequent alkylation by terminal ethylenic and acetylenic compounds can realized by one-pot reactions under sonication in the presence of atmospheric oxygen and the only precautionary measure due to the use of poisonous phosphine is to operate in an fume cupboard and the *in situ* generated PH_3 is consummated as soon as it is formed.

Acknowledgments : We are grateful to *the Centre National de la Recherche Scientifique (CNRS) and the Conseil Régional de la Région Midi-Pyrénées* for financial support.

References and notes

1. Gengembre, P. *Mém. Acad.*, **1785**, *10*, 651.
2. a) DE-PS 2 632 316, Hoechst AG, **1976**. b)Weferling, N. *Phosphorus and Sulfur*, **1987**, *30*, 641-644.
3. a) Hackspill, L.; Besson, J.; Herold A. in *Chimie Minérale*, PUF Ed., 2° Edition, **1964**, *1*, 617. b) Van Wazer, J. R. in *Phosphorus and its Compounds*, Interscience, New York, **1958**, *1*, 180 . c) Rauhut, M. M. in *Topics in Phosphorus Chemistry: Synthesis of Organophosphorus Compounds from Elemental Phosphorus*, Grayson, M. and Griffith, E. J. Editors, Wiley-Interscience, **1964**, *1*,1-16. d) Grayson, M.; Bartkus, E. A., *Pure Appl. Chem.* **1964**, *9*, 193. e) Maier, L. in *Topics in Current Chemistry: Synthesis of Organic Phosphorus Compounds from Elemental Phosphorus*, Springer-Verlag, **1971**, *19*, 1-59. f) Kosolapoff, G. M.; Maier, L. in *Organic Phosphorus Compounds*, Wiley-Interscience, **1972**, *1*, 1-287. g) Greenwood, N. N.; Earnshaw, A. in *Chemistry of the Elements*, Pergamon Press, **1984**, pp. 559 and 587-591. h) Corbridge, D. E. C. in *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology* Elsevier Science Publish., Third Edition, **1985**, p. 50-51.
4. J01068475 A, UMENO M, Jpn. Patent, **1989**.
5. a) Schroetter, M. A. *Annales de Chimie et de Physique*, **1848**, *XXIV*. b) Fremy, M. in *Encyclopédie Chimique: Métalloïdes*, Dunod Ed., Paris, **1883**, *II*, 280-282.
6. Amorphous red phosphorus was purshased from Prolabo or Aldrich and was used as received unless other wise stated. One-pot reactions were performed in the presence of atmospheric oxygen (air). In contrast, the two-steps reactions were realized under argon.
7. a) Rauhut, M. M.; Hechenbleikner, I.; Currier, H. A.; Schaefer, F. C.; Wystrach, V. P. *J. Am. Chem. Soc.* **1959**, *81*, 1103-1107. b) Bookham, J. L.; McFarlane, W.; Colquhoun, I. J. *J. Chem. Soc., Chem.Commun.* **1986**, 1041-1042.
8. Wolfsberger, Von W. *Chem. Zeit.* **1988**, *112*, 215-221.
9. a) Suslick, K. S. in *Ultrasound: Its Chemical, Physical, and Biological Effects*, VCH publishers, 1988. b) Lorimer, J. P.; Mason, T. J. *Chem. Soc. Rev.* **1987**, *16*, 239-274. c) Etemad-Moghadam, G.; Rifqui, M.; Layrolle, P.; Berlan, J.; Koenig, M. *Tetrahedron Letters*, **1991**, *32*, 5965-5968.
10. Trofimov, B. A.; Gusarova, N. K.; Malysheva, S. F.; Rakhmatulina, T. N.; Polubentsev, A. V.; Voronkov, M. G. *Zh. Obshch. Khim.* **1990**, *60*, 456.
11. Hubert, C.; Oussaid, B.; Etemad-Moghadam, G.; Koenig, M.; Garrigues, B. *Synthesis*, **1994**, 51-55.
12. a) Cristau, H. J.; Pascal, J.; Plenat, F. *Tetrahedron Letters*, **1990**, *31*, 5463-5466.

    b) Dorfman,Ya. A.; Aleshkova, M. M.; Karinskaya, A. S.; Borangazieva, A. K.; Kebekbaeva, M. M. *J. Gen. Chem. USSR*, **1991**, *61*, 999-1008.

(*Received in France* 6 *December* 1993; *accepted* 15 *March* 1994)