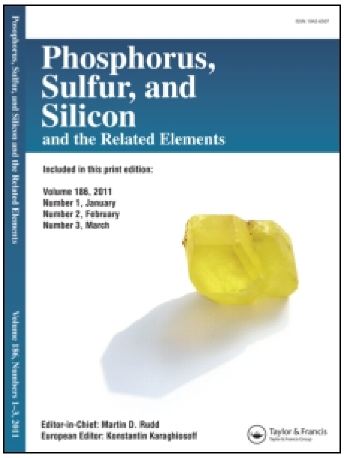


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactivity of N Phenyl Iminophosphoranes Towards Ozone: Evidence of Trioxo Azaphospholane Intermediates

Fayez El Khatib; Jacques Bellan; Max Koenig

To cite this Article Khatib, Fayez El , Bellan, Jacques and Koenig, Max(1998) 'Reactivity of N Phenyl Iminophosphoranes Towards Ozone: Evidence of Trioxo Azaphospholane Intermediates', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 391 — 398

To link to this Article: DOI: 10.1080/10426509808545479

URL: http://dx.doi.org/10.1080/10426509808545479

Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 391-398
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam N.V. Published under license by
the Gordon & Breach Science Publishers imprint.
Printed in Malaysia

REACTIVITY OF N PHENYL IMINOPHOSPHORANES TOWARDS OZONE: EVIDENCE OF TRIOXO AZAPHOSPHOLANE INTERMEDIATES

FAYEZ EL KHATIB[a], JACQUES BELLAN[b] and MAX KOENIG[c]*

[a]*Department of Chemistry, Faculty of Science, Jerash University, Jerash -Jordan,* [b]*UPRESA CNRS n°5068 and* [c]*Laboratoire d'Hétérochimie Fondamentale et Appliquée.UPRESA CNRS n°5069. Université Paul Sabatier. 31062 Toulouse Cedex -France*

(Received 29 January, 1998)

The ozonation of N-phenyl-iminophosphoranes $R_3P{=}NPh$ **1a-b** leads, after the P-N bond breakage, to the corresponding phosphorus oxides **2a-b** with the formation of complex adducts **3a-b** which precipitate at room temperature. The stoichiometry and the reaction mechanism depend on the nature of substituents R linked to the phosphorus atom. For R=Ph we detected the phosphonium intermediate **5a**, whereas for R=OEt the trioxoazaphospholanes **7b-9b** were characterized by ^{31}P NMR.

Keywords: Iminophosphoranes; ozone; phosphine oxide; phosphonium; trioxoazaphospholane

INTRODUCTION

The ozonation of unsaturated compounds containing nitrogen as imines[1] or ketoximes[2] have been extensively studied. Much attention has been devoted to the study of oxidation reactions of unsaturated organophosphorus compounds using activated forms of oxygen. Compounds such as ylides[3] and diphosphenes[4,5] react with ozone differently and these reactions had been fully studied. We present in this paper the reaction of phospha-λ^5 azenes with ozone at low temperature, using the ^{31}P NMR spectroscopy to identify the different intermediates formed.

---

* Corresponding Author.

RESULTS AND DISCUSSION

Phospha-λ^5 azenes **1a-b** containing unsaturated bonds P=N react in solution of dichloromethane with ozone at low temperature.The stoichiometry of the addition is dependent on the nature of the substituents linked to the phosphorus atom: O_3/**1a** = 3 and O_3 /**1b** = 2 .The observed intermediates decompose at room temperature leading to the corresponding oxides **2a-b** and complex precipitates **3a-b** which were isolated (scheme 1).

$$\underset{\textbf{1 a-b}}{R_3P{=}NPh} + n\,O_3 \longrightarrow \underset{\textbf{2 a-b}}{R_3P{=}O} + \left\{ \underset{\textbf{3 a-b}}{R_3P{=}O\,,\left(C_6H_5NO_x\right)_x} \right\}_y$$

a R = Ph n = 3 x = 4

b R = EtO n = 2 x = 3

SCHEME 1

1 – Ozonation of 1a

Ozone reacts in CH_2Cl_2 with N-phenyl-P,P,P triphenyl phosphin-λ^5 azene **1a** at –78°C. Under these conditions three molecules of ozone react with one molecule of the P=N compound.When the solution rises to room temperature the P-N bond is completely broken to yield triphenylphosphine oxide **2a** [δ ^{31}P =30 (CH_2Cl_2)] and a phosphorus complex adduct **3a** [δ ^{31} P =35 (CH_2Cl_2)] which precipitates.The precipitate is filtered and redissolved in a polar solvent (DMF). The ^{31}P NMR spectrum shows a unique signal [δ^{31}P = 35 (DMF)].The mass spectrum of **3a** indicates the presence of triphenyl phosphine oxide (m/z = 278).When the complex adduct solution in DMF is heated during one week at 120 °C, the phosphorus adduct is decomplexed and a unique signal characteristic of free $(C_6H_5)_3P$=-O [δ^{31}P = 25 (DMF)] is obtained in the NMR spectrum.

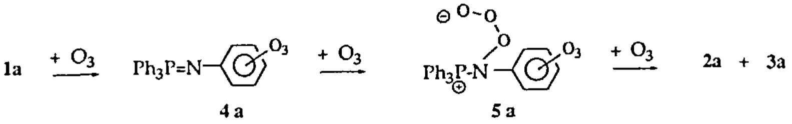
This result is confirmed by IR spectroscopy (νP=O = 1185 cm^{-1}). This band is not observed in the case of the unheated precipitate, it appears only after heating.

In order to detect the various intermediates, we have observed by ^{31}P NMR at low temperature the reaction of different amounts of ozone (one to three molecules) with constant amount of the P=N compound:

i. When less than one mole of ozone is absorbed at low temperature in the solution of the iminophosphorane **1a** [$\delta^{31}P = 4.4$ (CH_2Cl_2)], any modification appear in the ^{31}P NMR spectrum : we conclude that the P=N bond is not affected at low temperature and ozone is fixed on the phenyl substituent of **4a**.

ii. When the number of moles of ozone used is between one and two, the P=N bond begins to be broken and a phosphonium intermediate **5a** is formed. We detected a single signal with a characteristic chemical shift [$\delta^{31}P = 40$ (CH_2Cl_2)].

iii. When more than two moles of ozone were used, the P-N bond is completely broken ,the phosphonium intermediate **5a** disappears to yield the isolated **2a** and **3a** via the probable but undetected intermediate **6a** (scheme 2).



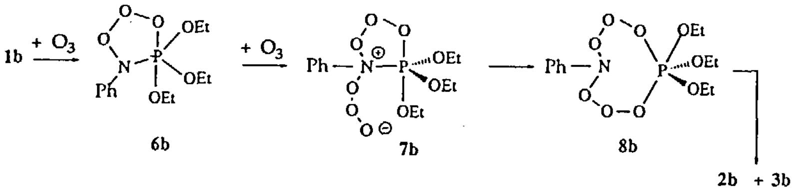
SCHEME 2

2 - Ozonation of 1b

Ozone react with N-phenyl-P,P,P-triethoxyphosphin-λ^5 azene **1b** in dichloromethane at –78°C with a stoichiometry O_3 / **1b** = 2 . During the reaction, a change of color has been observed.

At low temperature the reaction mixture is homogeneous and when the temperature is raised to room temperature, a very exothermic reaction takes place leading to the formation of a brown precipitate **3b** similar to **3a**. As previously we have detected at low temperature the formation of the intermediates which appear at different stoichiometry:.

i. When the stoichiometry O_3 /**1b** is 0.7 we observe in the ^{31}P NMR spectrum the disappearance of 70% of the starting material and the formation of triethoxy phosphoric ester **2b**($\delta^{31}P = -1$) and the formation of pentacoordinated phosphorus intermediates at $\delta^{31}P = -28.3$, -29.1) (Scheme 3). When the temperature of the reaction mixture is raised to room temperature the signals corresponding to the intermediates disappeared, while the starting material reacts completely. Only the triethoxy phosphoric ester and the precipitate formed are isolated.



SCHEME 3

ii. When the stoichiometry O_3/ **1b** is 1.6 . At low temperature, the starting material reacts completely. The major product obtained is the phosphoric ester accompanied by 50% of intermediates. At room temperature, the intermediate products decompose yielding the same products as above.

iii. When the stoichiometry O_3 / **1b** = 2, we observe besides to the above products a new intermediate at $\delta^{31}P = -53$ and $\delta^{31}P = -59$. We attribute this increase of the chemical shift to the formation of the probable hexacoordinate phosphorus intermediate also observed in the case of the ozonation of phosphites[6].

At room temperature, we observe the instantaneous formation of the phosphoric ester and its complex which precipitates.

3 - Discussion

Once the P=N bond is broken, as in the ozonation of Schiff bases, we expected the formation of nitrobenzene as an oxidation product[7]. Thus, Corey and coll. prepared nitroalkanes by ozonation of the corresponding phosphine imine.[8] But the result obtained shows that nitrobenzene is not formed at all, instead a precipitate is formed which is isolated and analysed. The results show also that the phenyl group linked to nitrogen is oxidized first with formation of OH and OOH groups which complex the triphenyl phosphine oxide by hydrogen bonding[9].

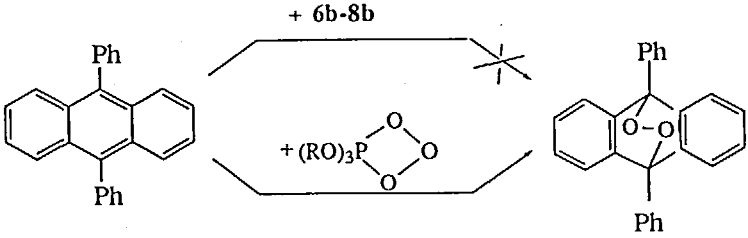
The relative ^{31}P NMR shift observed is the consequence of the variation of the P-O polarisation.This general effect was used in particular by Gutmann for the quantitative measurement of the acceptor properties of the solvents [10].

The reaction mixture [**1a**+ $3O_3$] oxidizes at low temperature three equivalents af n-butylphosphine to yield phosphine oxide and the phosphinate with 75/25 ratio. The precipitate formed is a strong oxidant agent because of the presence of great quantities of peroxidic or nitroso moieties[11] (Scheme 4).

$$3a + 3\,Bu_3P \longrightarrow Bu_3P{=}O + Bu_2P(O)OBu$$

SCHEME 4

Similarly,the proposed intermediates [**1b**+ 2 O_3] are strong oxidants, they oxydise triphenylphosphine but don't generate singlet oxygen like other kinds of ozonides such as trioxophosphetane[12] (Scheme 5)



SCHEME 5

The two isolated precipitate **3a** and **3b** have different stoichiometry.

The elemental analysis of the precipitate **3a** confirms the presence of triphenyl phosphine oxide and a large amount of oxygen (30%). This corresponds to the empirical formula $[(C_6H_5)_3PO, 4(C_6H_5NO_4)]n\cdot$

The ^1H NMR spectrum of the precipitate **3b** dissolved in DMF, indicates the presence of $(C_2H_5O)_3P{=}O$ and a large amount of hydroxyl groups. This result is confirmed by the IR spectrum.

The ^{31}P NMR spectrum shows only one phosphorus signal corresponding to $(C_2H_5O)_3P{=}O$. The precipitate is probably a peroxidic oligomer of the nitrogen compound which forms a complex with $(C_2H_5O)_3P{=}O$. With

3a, when the precipitate is heated, we observe the appearance of an IR band $\nu = 1270\ \mathrm{cm}^{-1}$ corresponding to a P=O bond. This band is not observed in the case of the unheated precipitate.The elemental analysis of the precipitate indicates the presence of a large amount of oxygen, the empirical formula is $[(C_2H_5O)_3P{=}O, 3(C_6H_5NO_3))_n$.

The mechanism of the ozonolysis of the P=N double bond is directly dependent on the substituents linked to phosphorus; in the case of **1a**, the three aryl substituents stabilize the positive charge of the phosphonium intermediate by delocalization whereas the presence of the ethoxy groups in **1b** enhances the Lewis acidity of the phosphorus atom and stabilizes preferentially the penta or hexacoordinated intermediates.

CONCLUSION

The reaction of ozone with the phospha-λ^5 azene depends on the nature of substituents linked to phosphorus.

The ozonation of **1a** takes place first on the phenyl ring bonded to nitrogen.The second step is the addition of one mole of ozone to the P=N double bond, leading to the stabilized phosphonium intermediate. A third mole of ozone reacts with this intermediate breaking the P-N bond and bringing about the formation of the oligomeric complex adduct.

For **1b** the electron withdrawing effect of the ethoxy substituents modifies the P=N strength and the Lewis acidity of the phosphorus atom. Only two molecules of ozone are needed for the breaking of the P-N bond via the pentacoordinated or hexacoordinated intermediates.

In both cases a brown precipitate is formed when the temperature of the reaction mixture is raised to room temperature. These precipitates are peroxidic oligomers stabilized by complexation with the oxidized phosphorus moieties.

EXPERIMENTAL SECTION

NMR spectra were obtained either on Brucker WH 90 or a Brucker AC 80. IR spectra were recorded on a Perkin Elmer 283. Mass spectra were recorded on a Varian MAT311A. Ozonisations were carried out using Ozonator Trailigaz Lab 76.

Ozonation Technique

Standard ozonisation: Oxygen debit 200L/h, pressure 0.5 bar, Power 1.15 A . In these conditions, we obtain ozone with a standard concentration of 8×10^{-4} mole of ozone per litre. The stoichiometry of the reaction can be determined, upon the completion of the reaction, after that the solution was flushed with a stream of argon and the unreacted ozone was titrated by iodometry.

Preparation of N-phenyltriphenyliminophosphorane 1a

Phenyl azide (4.165 g, 3.5 10^{-2} mol) was added slowly at room temperature to a stirred solution of triphenylphosphine (9.17 g, 3.5 10^{-2} mol) dissolved in 100 mL of toluene, under argon. Nitrogen was evolved and stirring continued for 2 hours. The solvent was evaporated under reduced pressure. **1a** was obtained in solid state with quantitative yield. $\delta^{31}P = 4.4$.

Preparation of N-phenyltriethoxyiminophosphorane 1b

Phenyl azide (4.165 g, 3.5 10^{-2} mol) was added to a stirred solution of triethylphosphite (5.81 g, 3.5 10^{-2} mol) dissolved in 100 mL of toluene, under argon. The mixture was heated at 100 °C for 3 hours. The solvent was evapored under reduced pressure and the phosphorane **1b** was obtained with quantitative yield. $\delta^{31}P = 1.6$.

Ozonation of N-Phenyltriphenyliminophosporane 1a

1a (0.322 g 0.91 10^{-3} mole) dissolved in 5 mL of dichloromethane, reacts with ozone at –78 °C. The reaction was carried out with the following stoichiometry O_3/**1a** = 0.5, 1.2 and 3. ^{31}P NMR spectra were recorded at different temperatures –70 °C, –50 °C, –10 °C and at room temperature. The precipitate **3a** obtained at room temperature is dried and isolated in solid form (yield = 25–30% relative to the total weight) $\delta^{31}P$ (DMF) = 35. IR (KBr) $\nu = 3300\ cm^{-1}$, $\nu = 1700\ cm^{-1}$. Anal. Calcd for $C_{42}H_{35}O_{17}N_4P$: C, 56.12 ; H, 3.90 ; N 6.24 ; O, 30.29 ; P, 3.43. Found : C, 55.81 ; H, 4.08 ; N, 5.82 ; O, 30.35 ; P, 3.40%.

Ozonation of N-phenyltriethoxyiminophosphorane 1b

1b (0.129 g, 5 10^{-4} mole) dissolved in 2 mL of C_7D_8 reacts at −78 °C with 0.7, 1.6 and 2 equivalents of ozone .With stoichiometry O_3/**1b** = 0.7 the ^{31}P NMR spectrum is recorded at −72 °C. When the temperature rises, modifications were observed. At room temperature precipitate **3b** is isolated $\delta^{31}P$ (DMSO) = −1.6. The filtrate is dried and dissolved in $CDCl_3$, the ^1H and ^{31}P NMR spectra are those of $(C_2H_5O)_3P{=}O$ **2b**. IR spectrum is recorded ($\nu_{P\text{-}O}$ = 1270 cm^{-1}). The weight of the precipitate **3b** obtained from stoichiometry O_3/**1b** = 2 represents 21%) of the total weight. IR spectrum of the precipitate **3b** is recorded ($\nu_{P\text{-}O\ bound}$ = 1240 cm^{-1}).

Anal. Calcd for $C_{18}H_{25}N_3O_{13}P$: C, 41.38 ; H, 4.79 ; N 8.05 ; O, 39.35 ; P, 5.94. Found : C, 41.97 ; H, 4.78 ; N, 7.72 ; O, 39.88 ; P, 5.83%.

References

[1] P.S. Bailey, Ozonation in Organic Chemistry, Academic Press, New York (1982).

[2] K. Griesbaum, X. Lin, A. Kassiaris and M. Scherer Liebigs Ann., 1381, (1997).

[3] F. El Khatib, A.M. Caminade and M. Koenig *Phosphorus and sulfur,* **14**, 381 (1983).

[4] A.M. Caminade, C. Couret, J. Escudié and M. Koenig *Chem.Comm.,*1622 (1984).

[5] F. El Khatib, A.M. Caminade, C. Ades M. Verrier, N. Paillous and M. Koenig *Phosphorus and Sulfur,* **26**, 91 (1986).

[6] F. El Khatib, A.M. Caminade and M. Koenig *Phosphorus and Sulfur,* **20**, 55 (1984).

[7] A.H. Riebel, R.E. Erickson, C.J. Abshire and P.S. Bailey, *J. Am. Chem. Soc* **82**, 1801 (1960).

[8] E J Corey, B. Samuelsson et F.A. Luzzio *J. Amer. Chem. Soc.,* **106**, 3682 (1984).

[9] a) R.D. Termple, Y. Truno et J.E. Lefflet *J. Amer. Chem. Soc.,* **85**, 249 (1963).

b) D.B. Cople, F. Fairlrother, J.R. Miller et A. Thompson *Proceeding of Chem. Soc.,* **300** (1964).

c) V. H. J. Haupt, F. Huber, C. Krüger, H. Preut et D. Thierbach Z. *Anorg. Allg. Chem.,* **436**, 229 (1977).

[10] V. Gutmann *Electrochimica Acta,* **21**, 661 (1976).

[11] J.I.G. Cadogan. *Quart. Rev.,* **22**, 222 (1968).

[12] F. El Khatib, A.M. Caminade, J.M. Aubry and M. Koenig *Canadian Journal of Chemistry,* **63**, 3203 (1985).