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Labile P–C bonds: *P*-(phosphinoyl)methyl-λ^5-phosphazenes and related compounds

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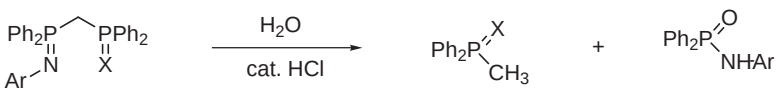
Abstract—*N*-Aryl-*P*,*P*-diphenyl-*P*-(diphenylphosphinoyl)methyl-λ^5-phosphazenes undergo smooth acid-catalysed hydrolysis with concomitant P–C bond fission yielding *N*-aryl-*P*,*P*-diphenylphosphinamides and diphenylmethylphosphane oxide. A tentative mechanistic explanation is given.

The literature quotes several instances of the cleavage of single P–C bonds by the action of metals or strong bases.[1] An archetypal example is the treatment of tertiary phosphanes with an alkali metal to provide secondary phosphide anions. Phosphane oxides and sulphides are known to behave similarly in the presence of strong bases.[2] Alkaline hydrolysis of phosphonium salts, generally affording phosphane oxides and hydrocarbons, is a typical example of single P–C bond cleavage by nucleophilic substitution at tetracoordinated phosphorus.[3]

In the course of a program devoted to the synthesis of new heteroditopic ligands for use in coordination and organometallic chemistry, we have recently reported[4] the preparation of a series of *N*-aryl-*P*,*P*-diphenyl-*P*-(diphenylphosphinoyl)methyl-λ^5-phosphazenes **1a**, formerly unknown compounds, which belong to the class of bis(oxidized) bis(diphenylphosphino)methane (dppm) derivatives. Herein we disclose that compounds **1a** and their thioanalogous **1b** undergo an easy fragmentation by P–C bond fission under mild hydrolytic conditions.

When $CDCl_3$ solutions of **1a** were monitored by ^1H and ^{31}P NMR we noted, after some hours, the rise of low intensity signals well differentiated from that attributed to **1a**. The intensity of the new signals increased with time, with the concomitant decrease of those corresponding to **1a**. At the end of the process (total consumption of **1a**, typically after 20–25 days), the initial two doublets in the ^{31}P NMR of **1a** were cleanly replaced by two well-separated singlets appearing near 20 and 30 ppm. Column chromatography (SiO_2 gel; AcOEt and then AcOEt/EtOH, 8:2) allowed the separation of two compounds from the final $CDCl_3$ solution, which were unequivocally identified as diphenylmethylphosphane oxide **2a**[5] and the corresponding diphenylphosphinic acid anilide **3**,[6] on the basis of their analytical and spectroscopic data (Scheme 1).



1a X = O
1b X = S
1c X = N-Ar

2a X = O
2b X = S
2c X = N-Ar

3

Ar = C_6H_5, 4-$H_3CC_6H_4$, 4-$H_3COC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4

Scheme 1.

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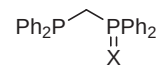
From the equation in Scheme 1 it is obvious that the fragmentation of **1a** into **2a** and **3** is in fact a hydrolytic process, and that the trace amounts of water contained in the $CDCl_3$ should be the actual responsible. However, we did not observe a similar fragmentation in other solvents such as wet DMSO-d_6, benzene or toluene. We then suspected that traces of HCl in the commercial $CDCl_3$ were also essential for promoting the hydrolytic fragmentation of **1a**. This was confirmed by adding a catalytic amount of 1N aqueous HCl to a refluxing solution of **1a** in wet $CHCl_3$, which ended in the virtually quantitative formation of **2a** and **3** after short reaction times (2–3 h).

In our hands, the sulphur analogous **1b** (Ar = 4-$H_3CC_6H_4$, 4-$H_3COC_6H_4$)[7] behaved similarly, giving rise to diphenylmethylphosphane sulphide **2b** and the corresponding phosphinamide **3**.

It has been reported[8] that di-λ^5-phosphazenes **1c** derived from dppm experimented acid-catalysed hydrolysis to give phosphanilides **3**, phosphane oxide **2a** and the corresponding aniline. In light of our present results, we presume these last two compounds come from the hydrolysis of the P=N function of the phosphazenes **2c**.

In summary, compounds of general structure **1** have been shown to fragment hydrolytically giving the species **2** and **3** by a rare P–C bond fission, which requires the catalytic action of HCl. It should be noted that other dppm derivatives, such as **4** and **5** depicted below, did not undergo this kind of fragmentation.



X = O, S, Se, NR

4

X, Y = O, S, Se

5

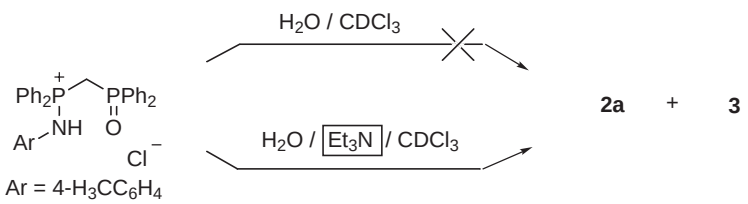
The two phosphorus atoms of the dppm fragment being at P(V) oxidation state and at least one of them in phosphazene form seem to be mandatory for the occurrence of the acid-catalysed fragmentation.

Concerning the sequence of chemical events leading to the P–C bond fission of compounds **1**, we reasoned that this sequence, promoted by the catalytic proton, should involve the initial protonation of the more basic centre in **1**, the nitrogen atom. This would lead to the aminophosphonium chlorides type **6**. In fact, when one equivalent of 10N aqueous HCl was added *at once*, at room temperature, to a chloroform solution of **1a** (Ar = 4-H_3C-C_6H_4), the salt **6** cleanly formed, which could be isolated and characterised. Obviously we next checked the evolution of **6** under the conditions in which the fragmentation of **1** occur. Unexpectedly, aminophosphonium chloride **6** remained unchanged for months in $CDCl_3$ solution or in refluxing wet $CHCl_3$ (Scheme 2). This result revealed that the *rapid and complete* conversion of **1a** into **6** blocked the fragmentation process.

However, the addition of one equivalent of Et_3N to the $CDCl_3$ solution of **6** cleanly converted it into **2a** and the corresponding **3** in less than 24 h. Most probably, the base is required for assisting the water addition to the P atom of the phosphonium function in **6**, the first step of the classical alkaline hydrolysis of phosphonium salts.[3] If the fragmentation of **6** follows the well-established mechanistic scheme of those hydrolytic reactions, the next step should be the detachment of one substituent (the best leaving group) from the pentacoordinated phosphorus of the resulting species, with the assistance of a base, thus yielding the new P=O bond.

On this basis, we believe that a reasonable sequence for explaining the acid-catalysed hydrolytic fragmentation of compounds **1** could be that represented in Scheme 3, a sort of reversible catalytic cycle in which **1** acts first as a base fixing the proton at its N atom, followed by nucleophilic attack of water to the most electrophilic P atom, assisted by **1** as base. The resulting pentacoordinated phosphorus species **7** is then cleaved, in an irreversible step, into **2** and **3**, a process facilitated by the action of the X atom of the P=X function as internal base and by the release of **2** as leaving group.

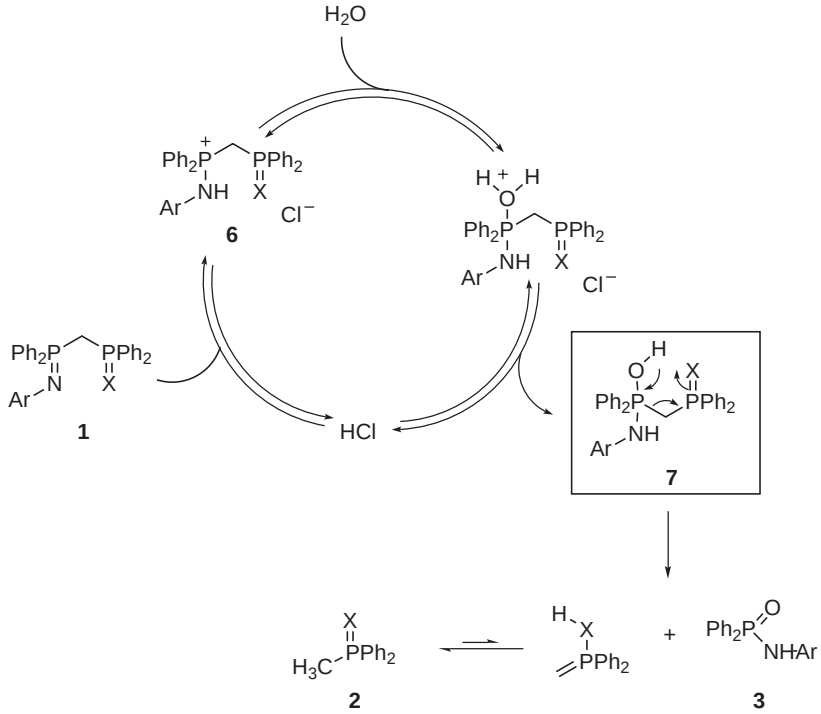
This tentative mechanistic scheme accounts for the most significant facts of the conversion of **1** into **2**+**3**, especially that only a catalytic amount of HCl is required, whereas the complete protonation of **1** by one equivalent of acid stops the process at the aminophosphonium salt **6**, providing no external base is added. While λ^5-phosphazenes are known to be easily cleaved to amines and phosphane oxides under acidic or basic hydrolytic conditions,[9] the fragmentation described here is relevant in following a notably different course. The previously reported fragmentation of tetraalkyl methylenediphosphonates and resembling species[10] may be mechanistically related to the one disclosed here.



Ar = 4-$H_3CC_6H_4$

6

Scheme 2.



Scheme 3.

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