First Evidence for a Curtius Type Rearrangement Involving a Charged Atom. An Easy Synthesis of an Iminophosphonium Salt

Michel Mulliez,[a] Jean-Pierre Majoral,[a] and Guy Bertrand[b]

[a] *Synthèse, Réactivité et Structure de Molécules Phosphorées, ERA 926, and* [b] *Laboratoire des Organométalliques, ERA 829, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cédex, France*

Irradiation of azidophosphonium salts $(Me_2N)_3P^+N_3,X^-$ (**1**; X = PF_6) and (**4**; X = Br) leads either to an iminophosphonium salt $(Me_2N)_2P^+{=}N{-}NMe_2,PF_6^-$ (**2**) or to an iminophosphorane $(Me_2N)_3P{=}NH$ (**7**) depending on the nature of the anion; these differences in the photochemical behaviour of (**1**) and (**4**) are rationalized by the transient existence of a phosphonitrenium salt $(Me_2N)_3P{=}N^+,X^-$ (**8**).

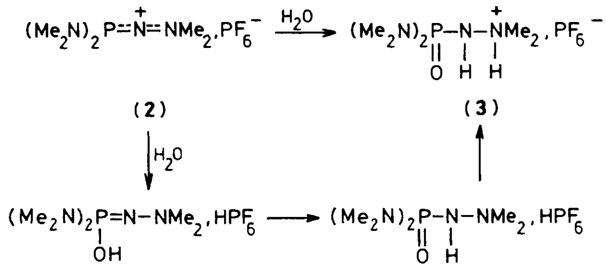
The Curtius rearrangement is a well known route to π-bonded nitrogen derivatives from the corresponding azides.[1] Various transient unusually hybridized organometallic species were obtained using this rearrangement which proved to be a general method allowing the co-ordination number of the atom bonded to the azido group to be decreased by one unit, keeping the number of valence bonds unchanged.[2]

However, all these reactions involve non-charged species. Here we report the synthesis of an unusually hybridized phosphorus cation from an azidophosphonium salt. This is the first example of a Curtius-type rearrangement involving a charged atom.

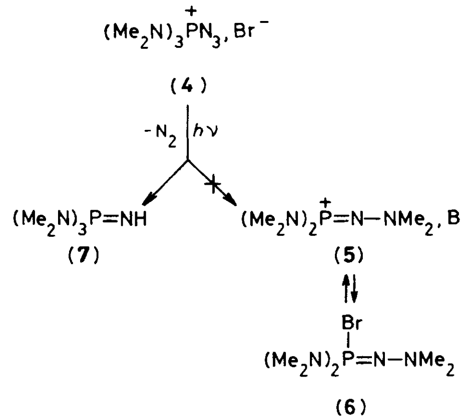
Irradiation of an acetonitrile solution (12 ml) of tris(dimethylamino)azidophosphonium hexafluorophosphate (**1**)[3] (350 mg, 10^{-3} mol), at 254 nm using a Rayonnet photochemical reactor (15 h, room temperature) gave the iminophosphonium salt (**2**)[†] with release of nitrogen.

$$\begin{array}{ccc} (Me_2N)_3P^+N_3,PF_6^- & \xrightarrow[-N_2]{h\nu} & (Me_2N)_2P^+{=}N{-}NMe_2,PF_6^- \\ (\mathbf{1}) & & (\mathbf{2a}) \\ & & \updownarrow \\ & & (Me_2N)_2P{-}N{=}N^+Me_2,PF_6^- \\ & & (\mathbf{2b}) \end{array}$$

After removal of the solvent (**2**) was obtained in quantitative yield as a very hygroscopic solid.[‡] Spectroscopic data suggest that the resonance forms (**2a**) and (**2b**) are of comparable importance: (i) a ^{1}H n.m.r. singlet at low field (δ 3.20, 6H); (ii) the ^{31}P chemical shift (+77 p.p.m.) compared with the δ values of trico-ordinated derivatives [$P(NMe_2)_3$ +123 p.p.m.] and those of previously reported iminophosphonium salts[4] [$(Me_2N)_2P^+{=}N{-}Ph,AlCl_4^-$ +41.7 p.p.m.].



Scheme 1

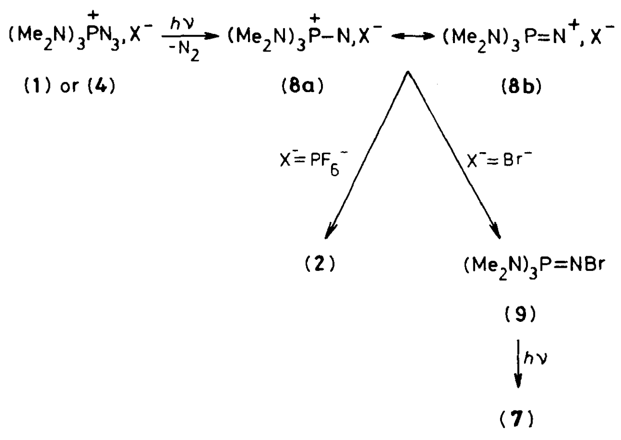


Scheme 2

Compound (**2**) is stable at room temperature only in a rigorously dry atmosphere, otherwise it gives rise to the hydrolysis product (**3**),[‡] most probably through initial nucleophilic attack of the positive phosphorus atom by the hydroxy group of water (Scheme 1).

[†] The synthesis of the first stable iminophosphonium salt (*via* addition of an organic azide to a phosphonium salt) was recently reported by Marre *et al.*[4]

[‡] All new compounds gave satisfactory spectroscopic data.



Scheme 3

In order to study the importance of the anion in a possible equilibrium between iminophosphonium salt (**5**) and the corresponding tetraco-ordinated pentavalent phosphorus derivative (**6**), tris(dimethylamino)azidophosphonium bromide (**4**) was irradiated as described above (Scheme 2). In fact we observed the formation of the iminophosphorane (**7**)[5] in 80% yield. This dramatic change in the course of the photolytic reaction, due to the nature of the anion, can be rationalized by two possible routes. The first would involve an equilibrium between the phosphonium salt (**4**) and the corresponding phosphorus(v) structure which would then have to undergo Curtius rearrangement with migration of bromine. However, to our knowledge, no precedent for bromine migration has been described in a Curtius type rearrangement. We prefer to postulate the transient existence of a phosphonium nitrene (**8a**) in resonance form with a phosphonitrenium salt (**8b**)§ (Scheme 3).

When the anion is a poor nucleophile such as PF_6^-, the intermediate (**8**) is stabilized by migration of a phosphorus substituent onto the nitrogen atom with formation of iminophosphonium salt (**2**). On the other hand, the good nucleophilicity of the bromine anion leads to the formation of derivative (**9**) containing a halogen–nitrogen bond. However this type of compound is very photolabile and on subsequent irradiation in acetonitrile, (**9**) is converted into the iminophosphorane (**7**).

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References

1 S. Pataï, 'The Chemistry of the Azido Group,' Wiley-Interscience, New York, 1971; W. Lwowski, 'Nitrenes,' Wiley-Interscience, New York, 1970; J. S. Thayer, *Organomet. Chem. Rev.*, 1966, **1**, 157.

2 A. Baceiredo, G. Bertrand, J. P. Majoral, and P. Mazerolles, *Nouv. J. Chim.*, 1983, **7**, 645; A. Baceiredo, G. Bertrand, and P. Mazerolles, *Tetrahedron Lett.*, 1981, **22**, 2553; A. Baceiredo, J. P. Majoral, and G. Bertrand, *Nouv. J. Chim.*, 1983, **4**, 255; J. P. Majoral, G. Bertrand, A. Baceiredo, and P. Mazerolles, *ACS Symposium Series*, 1981, **171**, 123; J. P. Majoral, G. Bertrand, A. Baceiredo, M. Mulliez, and R. Schmutzler, International Conference on Phosphorus Chemistry, Nice, September 1983; *Phosphorus Sulfur*, in the press.

3 B. Castro and J. R. Dormoy, *Bull. Soc. Chim. Fr.*, 1973, 3317.

4 M. R. Marre, M. Sanchez, and R. Wolf, *Phosphorus Sulfur*, 1982, **13**, 327; M. Sanchez, M. R. Marre, J. F. Brazier, J. Bellan, and R. Wolf, *ibid.*, 1983, **14**, 331.

5 J. Lorberth, *J. Organomet. Chem.*, 1974, **71**, 159.

6 T. Chivers, W. G. Laidlaw, R. T. Oakley, and M. Trsic, *J. Am. Chem. Soc.*, 1980, **102**, 5773 and references cited therein.

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§ Although no examples of stable nitrogen cations of type (**8**) have yet been reported, the well known cation $(Ph_3P)_2N^+$ is stable.[6]