PERKIN 2
COMMUNICATION

Structure and stability of oxaphosphetes formed as intermediates in the reaction of tertiary phosphine oxides and acetylenic derivatives

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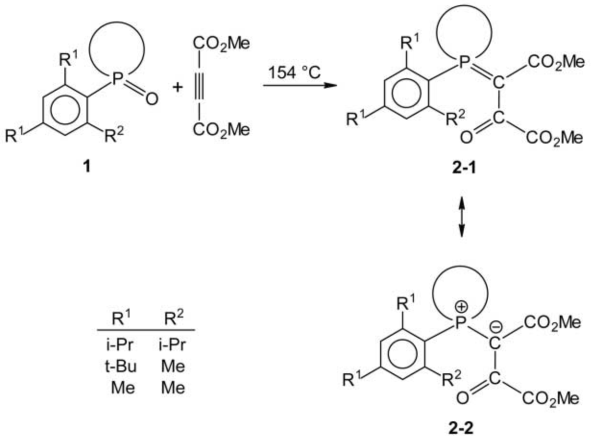
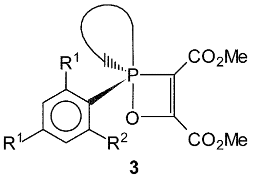
Quantum chemical calculations showed that oxaphosphetes with an equatorial oxygen atom may be intermediates in the reaction of acetylenic derivatives and phosphine oxides with electron-releasing substituent(s) on the phosphorus atom.

In previous studies it was found that the reaction of *P*-(2,4,6-trialkylphenyl) cyclic phosphine oxides (**1**) with dimethyl acetylenedicarboxylate (DMAD) afforded stabilised phosphonium ylides **2** (Scheme 1).[1]



Scheme 1

The products (**2**) with the 1,2-dihydrophosphole, 1,2,3,4-tetrahydrophosphole and 1,2-dihydrophosphinine moiety were presumably formed *via* the [2 + 2] cycloaddition of the P=O group and the acetylenic moiety of DMAD to furnish 1,2-oxaphosphetes (**3**) as the intermediates. In the beginning it was assumed that the oxaphosphetes of type **3** formed by an entirely new protocol may be stable species,[2] but later on quantum chemical calculations suggested that they are only intermediates.[1,3]



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In fact, 1,2-oxaphosphetes are the unsaturated derivatives of 1,2-oxaphosphetanes which are the intermediates of the Wittig reaction. Generally, the oxaphosphetanes can only be observed at low temperatures.[4] As unsaturated analogues, a stable 1,2-thiaphosphete[5] and some intermediate 1,2-azaphosphetes[6,7] have also been described. In a recent case, the four-membered ring species was found to equilibrate with the ring opened form.[8]

In this communication, the stability of the intermediates is described. PM3 semiempirical calculations[9] that were found to be particularly well suited to generate the geometrical data of phosphorus-containing systems[10] showed that the spirocyclic intermediates with an equatorial oxygen atom are more stable than those with an apical oxygen atom. As exemplified by the two forms of intermediate **4**, the value of the heat of formation is 41.3 kJ mol^{-1} higher for **4**$_1$ than for **4**$_2$ (Fig. 1) and both rings occupy an apical-equatorial position, while the sterically demanding *P*-aryl substituent is placed equatorially. The optimum geometry in the trigonal bipyramid around the phosphorus atom, $\alpha_{aa} = 180°$, $\alpha_{ee} = 120°$, while $\alpha_{ea} = 90°$, is somewhat distorted due to the rigid system. Species **4**$_1$ and **4**$_2$ seem to be real intermediates as they are placed on minima of the potential energy surface.

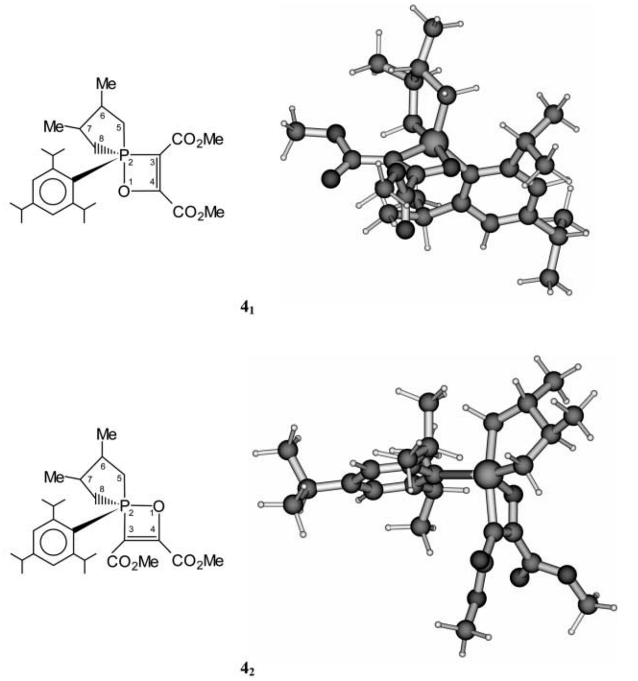

Fig. 1 Structure of intermediates **4**$_1$ and **4**$_2$ with selected bond angles (°) obtained by the PM3 method. For **4**$_1$: P_2–O_1–C_4: 89.8, O_1–C_4–C_3: 108.3, C_4–C_3–P_2: 93.5, O_1–P_2–C_5: 172.6, $C_{1'}$–P_2–C_5: 96.8, C_8–P_2–C_5: 92.4, C_3–P_2–C_5: 104.8, $C_{1'}$–P_2–O_1: 85.2, C_8–P_2–O_1: 92.7, C_3–P_2–O_1: 68.4, C_8–P_2–C_3: 108.6, $C_{1'}$–P_2–C_3: 124.4, $C_{1'}$–P_2–C_8: 121.1; for **4**$_2$: P_2–O_1–C_4: 95.0, O_1–C_4–C_3: 106.8, C_4–C_3–P_2: 88.5, C_3–P_2–C_5: 162.6, $C_{1'}$–P_2–C_5: 95.0, C_8–P_2–C_5: 91.4, O_1–P_2–C_5: 93.2, $C_{1'}$–P_2–C_3: 95.1, C_8–P_2–C_3: 93.2, O_1–P_2–C_3: 69.6, C_8–P_2–O_1: 111.5, $C_{1'}$–P_2–O_1: 117.8, $C_{1'}$–P_2–C_8: 129.8.

PM3 calculations showed that due to the increased instability of oxaphosphete **4**$_1$, the P–O bond cleavage is easier for this species (**4**$_1$) with an apical oxygen atom, than for **4**$_2$ with an equatorial oxygen.

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For oxaphosphete **5**, again the species with an equatorial oxygen atom proved to be more stable by PM3 semiempirical calculation. The geometry of intermediate **5** was optimised by the HF/6-31G* *ab initio* method.[11] The data shown in Fig. 2 matched quite well (±1–5%) those obtained by the PM3 method.

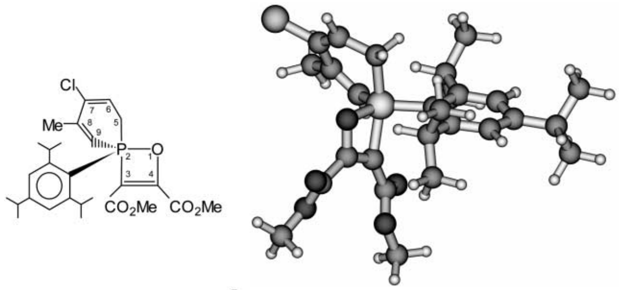

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Fig. 2 Structure of intermediate **5** with selected bond angles (°) obtained by the HF/6-31G* method. P_2–O_1–C_4: 95.1, O_1–C_4–C_3: 105.9, C_4–C_3–P_2: 88.0, C_3–P_2–C_5: 159.1, $C_{1'}$–P_2–C_5: 95.5, C_9–P_2–C_5: 96.2, O_1–P_2–C_5: 88.3, $C_{1'}$–P_2–C_3: 96.0, C_9–P_2–C_3: 93.4, O_1–P_2–C_3: 71.0, C_9–P_2–O_1: 112.0, $C_{1'}$–P_2–O_1: 128.3, $C_{1'}$–P_2–C_9: 118.8.

It was found that, especially in the case of intermediates with an axial oxygen atom, the conformation of the *ortho*-isopropyl groups affects highly the stability of the oxaphosphetes. If the geometry of the triisopropylphenyl group in isomer **4**$_2$ is adopted by species **4**$_1$, the oxaphosphete cannot be an intermediate, as according to the PM3 calculations, the four-membered ring opens up immediately. This sensitivity of the oxaphosphete ring with an apical oxygen atom (as *e.g.* in **4**$_1$) is attributed to steric factors. It can be seen that a minor structural modification in the conformation may determine if we have an intermediate or a transition state.

In the above cases, the novel [2 + 2] cycloaddition reaction between *P*-aryl phosphine oxides (**1**) and DMAD must have been promoted by the presence of the electron-releasing trialkylphenyl substituent on the phosphorus atom. The oxaphosphete intermediates obtained in the reaction of cyclic phosphine oxides **1** and DMAD are stabilised by the rupture of the P–O bond to afford stabilised phosphonium ylides (**2**). The energy gain is 33.5 kJ mol^{-1} for the ring opening of oxaphosphete **4**$_2$ according to the PM3 calculations. The driving force for the breaking of the P–O bond is the relief of the ring strain and the delocalisation in product **2**.

The most interesting finding was that even the interaction of trimethylphosphine oxide and acetylene may lead to the formation of an intermediate oxaphosphete (**6**). PM3 calculations at least suggested a relatively stable 2,2,2-trimethyl-1,2-oxaphosphete intermediate (**6**), where the oxygen atom is in the equatorial position. The stereostructure of oxaphosphete **6** together with relevant bond angles is shown in Fig. 3; the distortion of the optimum trigonal bipyramid is somewhat smaller than in the previous cases (**4**$_2$ and **5**).

The above theoretical results may indicate how to expand the scope of the novel [2 + 2] cycloaddition reaction. The interaction of trialkylphosphine oxides and different acetylene derivatives at elevated temperature and under pressure will also be tested during the next stage of our project.

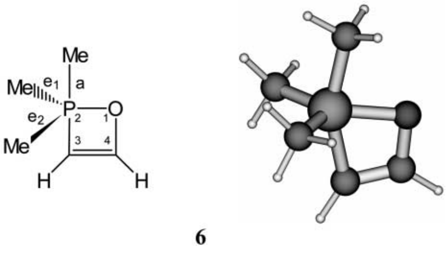

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Fig. 3 Structure of intermediate **6** with selected bond angles (°) obtained by the HF/6-31G* method. P_2–O_1–C_4: 94.6, O_1–C_4–C_3: 105.7, C_4–C_3–P_2: 88.0, C_a–P_2–C_3: 158.4, C_a–P_2–O_1: 86.7, C_a–P_2–C_{e1}: 96.2, C_a–P_2–C_{e2}: 96.2, C_3–P_2–O_1: 71.7, C_3–P_2–C_{e1}: 96.0, C_3–P_2–C_{e2}: 96.0, C_{e1}–P_2–O_1: 124.3, C_{e2}–P_2–O_1: 124.3, C_{e1}–P_2–C_{e2}: 110.8.

To compare the experimental and the calculated structures at the PM3 semiempirical level, calculations were performed on the structure of 1,2-λ^5-azaphosphete **7** (Fig. 4). Kano *et al.*[8] recently published the results of an X-ray crystallographic analysis for compound **7**.

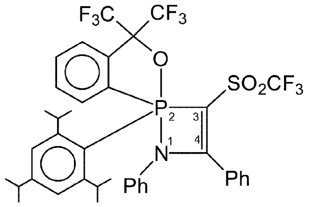

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Fig. 4 Selected bond lengths (Å) and angles (°) for 1,2-λ^5-azaphosphete **7** obtained by X-ray crystallographic analysis[8] and by the PM3 method (in parentheses): P_2–N_1: 2.170 (2.015), P_2–C_3: 1.815 (1.773), C_3–C_4: 1.415 (1.400), C_4–N_1: 1.314 (1.351), P_2–O: 1.676 (1.795), O–P_2–N_1: 169.0 (169.8), C_3–P_2–N_1: 66.8 (69.6), C_4–C_3–P_2: 99.9 (96.1), N_1–C_4–C_3: 107.1 (105.4).

The calculated structural parameters show an acceptable agreement with the experimentally obtained data for 1,2-λ^5-azaphosphete **7**,[8] which supports the application of the PM3 method for the calculation of analogous compounds.

Acknowledgements

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References

1 (*a*) Gy. Keglevich, H. Forintos, T. Körtvélyesi and L. Tőke, *J. Chem. Soc., Perkin Trans. 1*, 2002, 26; (*b*) Gy. Keglevich, T. Körtvélyesi, H. Forintos, Á. Gy. Vaskó, I. Vladiszlav and L. Tőke, *Tetrahedron*, 2002, **58**, 3721.
2 Gy. Keglevich, H. Forintos, Á. Szöllősy and L. Tőke, *Chem. Commun.*, 1999, 1423.
3 Gy. Keglevich, T. Körtvélyesi, H. Forintos, A. Tamás, K. Ludányi, V. Izvekov and L. Tőke, *Tetrahedron Lett.*, 2001, **42**, 4417.
4 E. Vedejs and C. F. Marth, in *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*, L. D. Quin and J. G. Verkade, eds., VCH, New York, 1994, Ch. 23, p. 297.
5 T. Kawashima, T. Iijama, H. Kikuchi and R. Okazaki, *Phosphorus, Sulfur Relat. Elem.*, 1999, **144–146**, 149.
6 T. Uchiyama, T. Fujimoto, A. Kakehi and I. Yamamoto, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1577.
7 N. Kano, J.-H. Xing, A. Kikuchi and T. Kawashima, *Heteroat. Chem.*, 2001, **12**, 282.
8 N. Kano, A. Kikuchi and T. Kawashima, *Chem. Commun.*, 2001, 2096.
9 J. J. P. Stewart, MOPAC93 (Revision V. 2), Fujitsu Ltd, Tokyo, 1995; the geometry was fully optimised (the gradient norm was less than 0.01); the force matrix was found to be a definite positive in the optimum structure.
10 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209; J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.
11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Clioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 98, Revision A. 6, Gaussian, Inc., Pittsburgh PA, 1998.