Generation of a Pentaco-ordinated Protonated Oxyphosphorane in Equilibrium with the Isomeric Enol Phosphonium Ion and Unprotonated Oxyphosphorane

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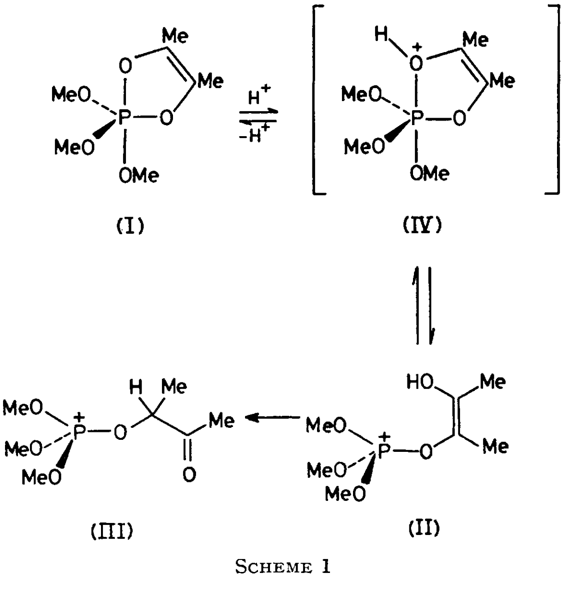
Summary Reaction of 2,2,2-trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholen with FSO_3H in CH_2Cl_2 at low temperatures gives the corresponding protonated oxyphosphorane.

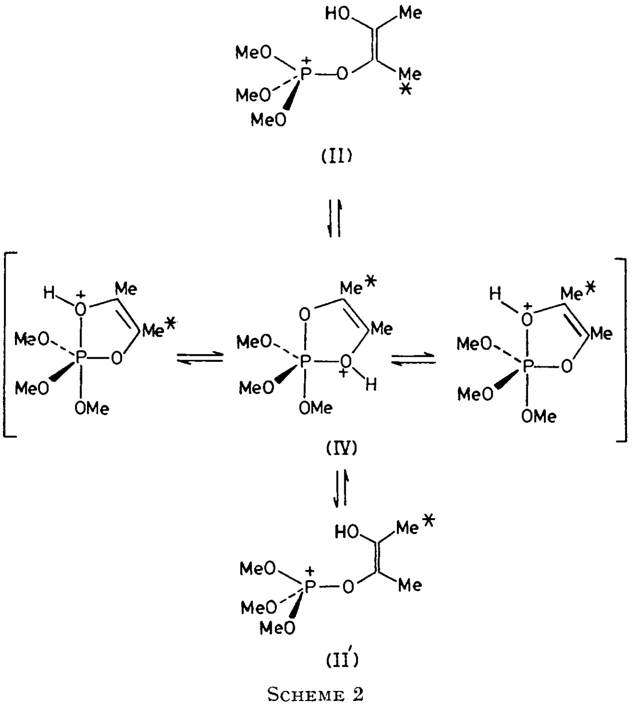
As a part of our investigations towards the intermediacy in group transfer reactions of pentavalent protonated phosphorus compounds[1] we have studied the generation and stability of the species under low nucleophilic conditions. Until now, little has been reported on the occurrence of such intermediates. Recently, Ramirez *et al.*[2] reported a protonated structure derived from a bicyclic oxyphosphorane. However, data regarding monocyclic compounds are lacking completely.

On addition of <1 equiv. of FSO_3H to a solution of 2,2,2-trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholen[3] (I) in CH_2Cl_2 (*ca.* 1 M), the ^{1}H n.m.r. spectrum at -100 °C shows, apart from the signals characteristic of (I) [δ 3·57 (OMe, J_{PH} 13 Hz) and 1·83 (Me)], resonances due to another species [δ 4·28 (OMe, J_{PH} 11·5 Hz), 1·95 (Me), and 7·92 (OH)] which are consistent with compound (II) the structure of which was confirmed by its ^{13}C and ^{31}P n.m.r. spectra. All n.m.r. spectra are temperature dependent; the ^{1}H n.m.r. spectrum at -80 °C shows a coalescence of the vinylic methyl groups of (I) and (II), whereas at -50 °C the corresponding methoxy doublets merge. At more elevated temperatures (up to 0 °C) a sharpening of all signals was observed. Consistent with the above observations, the ^{31}P and ^{13}C n.m.r. spectra of a mixture of both compounds showed, in the corresponding temperature range, line broadening effects. When the temperature is raised beyond 0 °C, the equilibrium vanishes as a consequence of an irreversible transformation of the enol (II) into the corresponding ketone (III). These observations indicate a dynamic equilibrium between (I) and (II) as shown in Scheme 1, as a result of an intermolecular proton transfer. This reversible proton transfer, which involves concomitantly rupture of the P–O linkage of (I) and ring closure of (II), is most adequately explained by assuming the rate determining intermediacy of the protonated oxaphospholen (IV). This is confirmed by the Gibbs free energy of activation, which can be estimated from line broadening effects at 12·7 kJ. This figure is close to that found for proton transfer reactions which also involve oxonium ions.[4]

Addition of 1 equiv. of FSO_3H to a solution of (I) in CH_2Cl_2 results in complete conversion of (I) into (II) as revealed by ^{1}H, ^{13}C, and ^{31}P n.m.r. spectroscopy. The ^{1}H n.m.r. spectrum at -100 °C shows a sharp doublet for the methoxy protons and a broadened singlet for the vinylic methyl groups. The line broadening of the latter signal was cancelled at -80 °C. Similarly, the ^{13}C n.m.r. spectrum shows sharp signals for the methoxy groups and line broadening for the other resonances in the temperature range from -100 to 0 °C. Moreover, the difference between the chemical shifts of the two vinyl methyl groups decreases. The apparent interchange of the two vinylic methyl groups can only be explained by assuming a different equilibrium as depicted in Scheme 2. Similar to the mechanism described earlier, the protonated oxaphospholen (IV) occurs as an



SCHEME 1



SCHEME 2

intermediate which, after pseudorotation and an intramolecular proton transfer, gives rise to the isomer (II′). Quenching of the reaction mixtures described above with pyridine or trimethylamine at −70 °C afforded exclusively the starting compound (I). Finally, addition of >1 equiv. of FSO_3H to a solution of (I), immediately gives rise to an irreversible formation of (III), which indicates that the described equilibria can only be operative in the absence of free protons.

The experimental demonstration of the existence of an intermolecular dynamic equilibrium involving the protonated oxaphospholen (IV) supports the intermediates which are believed to form in the acid-catalysed equilibrium between hydroxyphosphorane and hydroxyphosphate.[2] The intramolecular process described in this work is similar to the mechanism of the cyclization of benzoxazaphospholine to iminophosphorane.[5]

Apparently, the ring closure of the enol (II) is a low-energy process since it is not the rate-determining step in the dynamics of the intermolecular exchange (*vide supra*). This is conceivable on the basis of the study of Dreiding models of (II) which show a close proximity of the enol oxygen to the phosphorus nucleus. Thus, the intermediate (IV) may be the reactive species in group transfer reactions also.

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[1] W. G. Voncken and H. M. Buck, *Rec. Trav. chim.*, 1974, **93**, 14, 210; W. G. Voncken, A. M. C. F. Castelijns, S. A. J. de Leeuw, and H. M. Buck, *Tetrahedron Letters*, 1977, **8**, 729.

[2] F. Ramirez, M. Nowakowski, and J. F. Marecek, *J. Amer. Chem. Soc.*, 1977, **99**, 4515.

[3] F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, 1963, **85**, 3252.

[4] A. Loewenstein and A. Szöke, *J. Amer. Chem. Soc.*, 1962, **84**, 1151.

[5] H. Stegmann, R. Haller, and K. Scheffler, *Chem. Ber.*, 1977, **110**, 3817.