Unexpected Reaction between Benzaldehyde and 2,4,4,5,5-Pentamethyl-1,3,2-dioxaphospholane leading to a Phospha(v)oxirane Dimer

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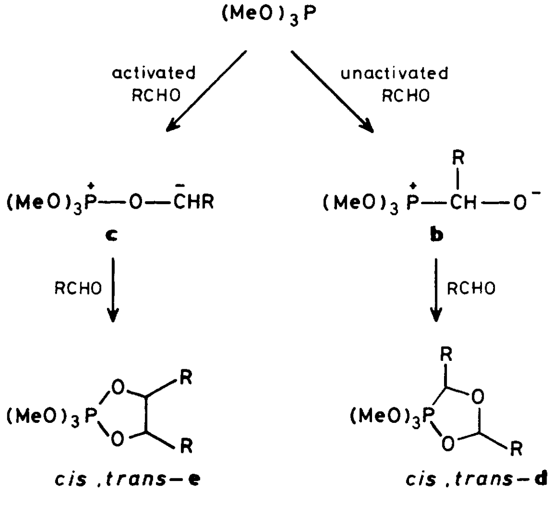
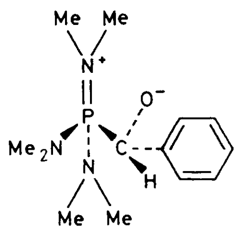
Benzaldehyde reacts with 2,4,4,5,5-pentamethyl-1,3,2-dioxaphospholane (**1**) to afford an oxaphosphirane (**2**) and its dimeric form dioxadiphosphorinane (**3**) in equilibrium.

It is known that benzaldehyde reacts with tricovalent phosphorus derivatives leading to either a 2:1 adduct (Scheme 1)[1,2] or a 1:1 adduct when it is stabilized as a zwitterionic species(I).[3] With α-ethylenic ketones, ylides or phosphoranes were obtained[4] (Scheme 2).

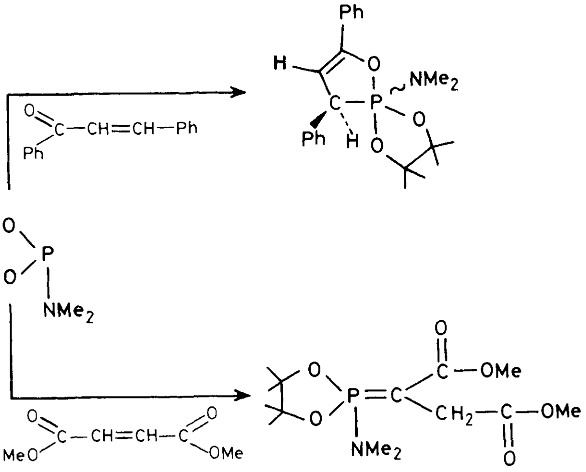
We report here the reaction between benzaldehyde and 2,4,4,5,5-pentamethyl-1,3,2-dioxaphospholane (**1**) in dichloromethane at room temperature, resulting in a white solid after addition of hexane [m.p. 184 °C (decomp.), 60%]. The remaining solution still contains a small amount of (**4**) and, when the solvent is not well degassed, the oxidation product of (**1**) (δ ^{31}P 40 p.p.m.). The elemental analyses of the new compound correspond to a 1:1 adduct.

This compound could be oxaphosphirane (**2a**) or one of its zwitterionic forms (**2b**) ($\geq\underset{|}{P}^{+}–C–O^{-}$ or (**2c**) ($\geq\underset{|}{P}^{+}–O–C^{-}$. ^{31}P-{^{1}H} n.m.r. spectra show a singlet near −25 p.p.m., whatever the solvent, the temperature, and the resonance frequency; without proton irradiation, a very complex signal is observed ($\Delta\nu_{1/2}$ ~41 Hz). Under irradiation at 1.28 p.p.m. {CH_3}, it becomes a broad triplet ($\Delta\nu_{1/2}$ ~21 Hz). When the temperature of the solution is varied, two noticeable features emerge. (i) A very slight variation of $\delta^{31}P$: in toluene $\Delta\delta P = -0.5$ p.p.m. between 294 and 193 K; in pyridine $\Delta\delta P = +0.17$ p.p.m. between 305 and 345 K. (ii) A slight decomposition of the sample at 330 K in pyridine; the extent of decomposition is about 30% after 80 min at 345 K. These data suggest that the equilibrium is shifted very much towards (**3**), and that the formation of (**2**) was not observed at higher temperatures because of its decomposition under our experimental conditions. ^{1}H n.m.r. spectra show a multiplet (1H) at about δ 6 which appears to consist of two doublets. This could be attributed to the two isomeric forms of the oxaphosphirane



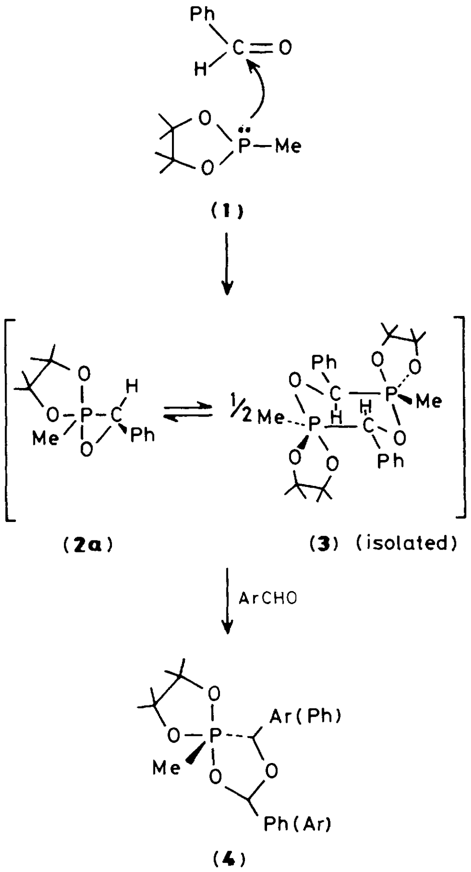


(I)



(2a). However, no alteration occurs on changing the resonance frequency (80 or 250 MHz), temperature (from +50 to −90 °C), or solvent (toluene, pyridine, chloroform), and the ^{1}H-{^{31}P} n.m.r. signal was only a singlet, so this explanation is unlikely. Furthermore, ^{13}C-{^{1}H} n.m.r. (20.3 and 75.47 MHz) spectra† are not consistent with an oxaphosphirane form (2a). Near δ 80, a dd signal (J_{CP} 131.6 and 8.2 Hz) attributed to a C-methine group (revealed by J. MOD. XH Bruker sequency) bonded to two magnetically inequivalent phosphorus atoms is observed.

These results prompted us to consider a centrosymmetric dimeric structure (3). The field desorption mass spectrum shows both monomeric and dimeric species,† and the ^{1}H n.m.r. signal mentioned above is consistent with the AA′ part of an AA′XX′ system formed by phosphorus atoms and methine protons. A resolution enhancement is obtained if the *ortho* protons of the phenyl groups are irradiated at a temperature of 45 °C: $^2J_{PH}$ (∓) 9.25, $^3J_{PH}$ = (±) 11.15, $^3J_{PP}$ 1.4, $^5J_{HH}$ 1.7 Hz. Only 1,4,2,5-dioxadiphosphorinane compounds with a tetraco-ordinated phosphorus atom are already known.[5,6] A crystal structure study of a tetraphosphonate potassium salt[6a] shows a chair conformation, with the P–C bonds lying in the same plane with oxygen atoms on both sides (a ±0.54 Å).



Reacting 4-MeC$_6$H$_4$CHO with dimer (3) (2 : 1) leads to the spirophosphorane (4) ($t_{1/2}$ ~15 min, C$_6$D$_6$, room temp.), a 2 : 1 adduct analogous with compounds **d** (Scheme 1) as shown by the n.m.r. spectra [δ ^{31}P −8.75 p.p.m.; δ ^{1}H 6.23 (d, $^3J_{PH}$ 4.3 Hz, CH) and 5.05 (d, $^2J_{PH}$ 13.8, Hz, CH)].‡ Moreover, the ^{31}P n.m.r. spectrum of the mixture (CDCl$_3$) obtained after a few minutes, shows several signals corresponding to the 2 : 1 adduct (4) and the starting phospholane (1) (202 p.p.m.) and its oxide (40 p.p.m.). These results and the mass spectrum† suggest an equilibrium between dimer and monomer (Scheme 3). The different reactivity of phosphites and cyclic phosphonites with aldehydes probably results from the dioxaphospholanyl ring which enhances the reactivity of (1) and stabilizes the pentacovalent forms (2a) and (3) relative to the two zwitterionic forms (2b) and (2c) proposed as intermediates by Ramirez.[2] Very recently Gorenstein has found, by *ab initio* M.O. calculations, that an oxaphosphirane with a pentacovalent phosphorus atom is an intermediate in the reaction of phosphorus acid with formaldehyde.[7] Heterophosphiranes (S or N as heteroatom) with a pentacovalent phosphorus atom have been isolated,[8,9] whereas the only isolated oxaphosphirane has a tetraco-ordinated phosphorus atom.[10,11] Nevertheless oxaphosphiranes with a pentacovalent phosphorus atom have been observed in equilibrium with the zwitterionic forms,[1,2,12] but not isolated. For several years, the phos-

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† *Spectral data* for (3): ^{1}H n.m.r. ([^{2}H$_5$] pyridine, 250 MHz) δ 7.84—7.16 (3 m, 2H, 2H, 1H, Ph), 5.97 (m, 1H), 1.28 (d, 3H, $^2J_{HP}$ 14.7 Hz, CH$_3$P), 1.25 and 1.15 [12H, (CH$_3$–C)$_4$]: broad signals which split into four peaks at 233 K, 1.62, 1.81, 2.02, and 2.06. ^{31}P-{^{1}H} N.m.r. (101.37 MHz) δ 25.0 (s) (pyridine, 305 K); −23.5 (s) (toluene, 294 K). ^{13}C N.m.r. (pyridine-C$_6$D$_6$, 20.3 MHz) δ 142, 129 (s), 127.8, 126.8 (d, J_{PC} 2.85, 3.3, 1.2, 1.8 Hz, Ph), 80.2 (d, $^1J_{PC}$ 131.6, $^2J_{PC}$ 8.2 Hz, CH), 78.5 (br., OCCO), 25.68 and 24.61 (CH$_3$–C), 21.53 (d, $^1J_{PC}$ 146.8 Hz, CH$_3$–P). M.s.: m/z 573 (M^+ + 2H$_2$O + 1), 555 (M^+ + H$_2$O + 1), 537 (M^+ + 1), 465, 287 (M^+/2 + H$_3$O), 269 (M^+/2 + 1), 162 (1) [peak intensities depend on filament heating; at the highest temperature, only monomer (m/z 269) is present].

‡ (4): ^{1}H N.m.r. (C$_6$D$_6$, 80 MHz) δ 7.75—7.00 (m, 9H, C$_6$H$_5$ and C$_6$H$_4$), 6.23 (d, $^3J_{PH}$ 4.3 Hz, CHOP), 5.05 (d, $^2J_{PH}$ 13.8, 1H, CH-P), 2.13 and 2.04 (3H, CH$_3$–C$_6$H$_4$), 1.46 (d, $^2J_{PH}$ 15.2 Hz), 1.42 (d, $^2J_{HP}$ 15.5, CH$_3$–P).

pha(v)-oxirane(**2**) has been invoked to explain a lot of reactions of phosphorus(III) compounds with aldehydes, particularly the Ramirez reaction of benzaldehyde with phosphites.

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