

Oxidation of Phosphanes with Orthoquinones: An Unusual Decomposition of an Unexpectedly Stable Zwitterion

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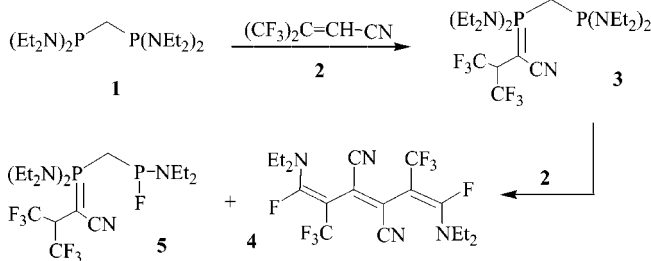
Oxidation of the ylide $(\text{Et}_2\text{N})_2\text{P}=\text{C}(\text{CN})\text{CH}(\text{CF}_3)_2\text{CH}_2\text{P}(\text{NEt}_2)_2$ (**3**) with tetrachloroorthobenzoquinone (TOB) does not give the expected 1,3,2-dioxaphospholane but stops at the formation of the unusually stable intermediate zwitterion **6**. The molecular structure of **6** was established by X-ray

analysis. In solution at temperatures above 15 °C zwitterion **6** undergoes an unusual decomposition into symmetrical carbodiphosphorane **7** and hexafluoroisovaleronitrile **8**.

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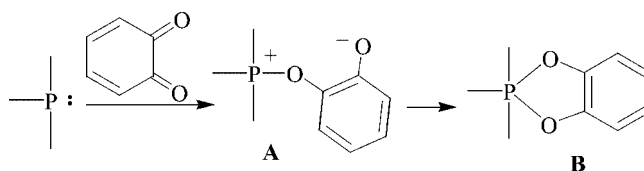
Introduction

Previously we have described the addition of 4,4,4-trifluoro-3-(trifluoromethyl)-2-butenenitrile (**2**) to bis[bis(dimethylamino)phosphanyl]methane (**1**) to give the monoylide **3**. The reaction of **3** with a second equivalent of **2** does not give the expected symmetrical diylide but leads unexpectedly to the almost quantitative formation of the fluorinated triene **4**.^[1,2] The second product of this reaction was identified as the fluorine-substituted ylide **5**. These two reactions can be combined in one and triene **4** can be easily prepared by adding two equivalents of **2** to the starting methylenediphosphane **1**.



The most probable route for formation of the symmetric molecule of triene **4** is the dimerization of the appropriate carbene, and the only possible way for this to form is by dissociation of the ylidic $\text{P}=\text{C}$ bond. We reasoned that if this is not a particular case, then an analogous cleavage may also be observed if the trivalent phosphorus atom of **3** were to react with other electrophilic reagents.

Here we wish to report on the rather unusual reaction of mono ylide **3** with tetrachloro-orthobenzoquinone (TOB). The oxidation of phosphanes with orthobenzoquinones normally leads to the formation of five-coordinate phosphoranes in which two oxygen atoms are connected to phosphorus to form 1,3,2-dioxaphospholane **B**. Such reactions proceed in two steps via intermediate zwitterionic compounds **A**, which are very unstable and can only be detected by NMR spectroscopy at low temperatures.^[3] The increase of steric hindrance stabilizes the zwitterionic intermediate. For example, the use of the more bulky phenanthrenequinone instead of benzoquinone in the reaction with triphenylphosphane gave the appropriate intermediate of type **A**, which is stable at room temperature.^[4] Unfortunately, X-ray investigation of this compound could not be performed.



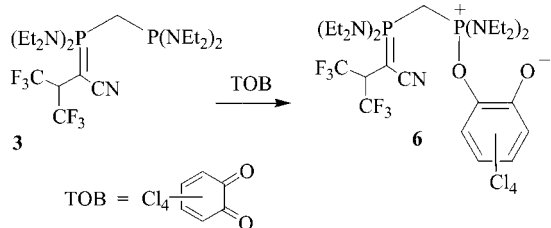
We have found that the reaction of compound **3** with TOB does not lead to the expected phosphorane structure, but stops at the formation of zwitterionic intermediate **6**. This compound crystallizes easily from the reaction mixture in diethyl ether in 65% yield as colorless crystals that turned out to be unusually stable. The detailed molecular structure of **6** (Figure 1) was established by X-ray analysis.

The bonding situation around phosphorus P(2) does not correspond to the trigonal-bipyramidal coordination geometry typical of a $\lambda^5\text{P}^5$ configuration but displays the tetrahedral geometry of the phosphonium structure $\lambda^4\text{P}^5$. The appearance of a positive charge at phosphorus P(2) causes some shortening of the $\text{P}(2)-\text{C}(1)$ bond in comparison with

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the starting compound **3** (179.5 and 187.6 pm, respectively). The negatively charged oxygen O(2) is situated between the two positively charged phosphorus atoms. The P(1)–O(2) and P(2)–O(2) distances (415.9 and 320.1 pm, respectively) are substantially longer than the P(2)–O(1) bond [157.93(19)], which excludes bonding between the atoms. The structure around the ylidic phosphorus P(1) does not differ substantially from that of the starting compound **3**. The two adjacent nitrogen atoms N(1) and N(2) have slightly different configuration. The N(1) atom is almost flat, whereas the N(2) atom has a more pronounced tetrahedral geometry [the sums of angles are 358.5(6)° and 348.0(1)°, respectively]. In solution, however, both diethylamino groups are equivalent and display common signals in the ^1H NMR spectrum.

The ylidic carbon C(10) has an ideal flat conformation accounting for the delocalization of the negative charge on the nitrile group. That is why the P(1)–C(10) bond (171.4 pm) is somewhat longer than a normal ylidic bond (168 pm),^[5] whereas the C(1)–C(2) distance is considerably shorter (139.7 pm) than the average single C–C bond. These data are consistent with the structure of the other nitrile-substituted phosphorus ylides.^[6–8]

Considering that the ylidic P(1)–C(10) bond is highly polarized, the molecule contains two positively charged phosphorus atoms and negatively charged oxygen and carbon atoms. The ^{31}P NMR spectrum of **6** displays two doublets

at $\delta = 44.51$ and 57.20 ppm ($^2J_{\text{P,P}} = 11.2$ Hz). These values are typical for ylidic and positively charged tetracoordinate phosphonium structures, respectively. If phosphorus P(2) were connected to the second oxygen O(2) it would have a five-coordinate phosphorane structure and a chemical shift of about $\delta = -50$ ppm. The methylene group between the two electron-withdrawing phosphonium centers displays a doublet of doublets at $\delta = 4.74$ ppm in the ^1H NMR spectrum. This value suggests that the acidity of the CH_2 protons is comparable with that of CH_2Cl_2 . In the presence of the adjacent anionic centers in the molecule this may lead to the appearance of other prototropic forms. Indeed, the ^1H NMR spectrum of compound **6** in chloroform displays a temperature-dependent equilibrium between zwitterionic form **6** and other possible forms **6a,b** resulting from the migration of one of the protons to the negatively charged oxygen O(2).

At +15 °C the position of the equilibrium is completely shifted to the zwitterionic form **6** and the P–CH₂–P methylene protons display a broad doublet of doublets at $\delta = 4.74$ ppm. At 0 °C two additional very broad signals at $\delta = 9.46$ and 2.46 ppm appear in the spectrum. The low-field signal belongs to the OH proton and the chemical shift value of the second one is more in agreement with the P=CH–P proton of isomer **6a**. This proton is connected to the negatively charged ylidic carbon atom and is thus shifted to higher field than that of structure **6b**. The intensity of the signals of the OH-containing isomers increases upon lowering the temperature. The contribution of structure **6b** probably increases at low temperature because the broad signal of the CH proton shifts gradually to lower field ($\delta_{\text{H}} = 2.94$ ppm at –40 °C). The ratio between isomers **6** and **6a,b** at this temperature reaches 40:60. We did not find signals for the fourth possible prototropic form **6c** in the ^1H NMR spectrum.

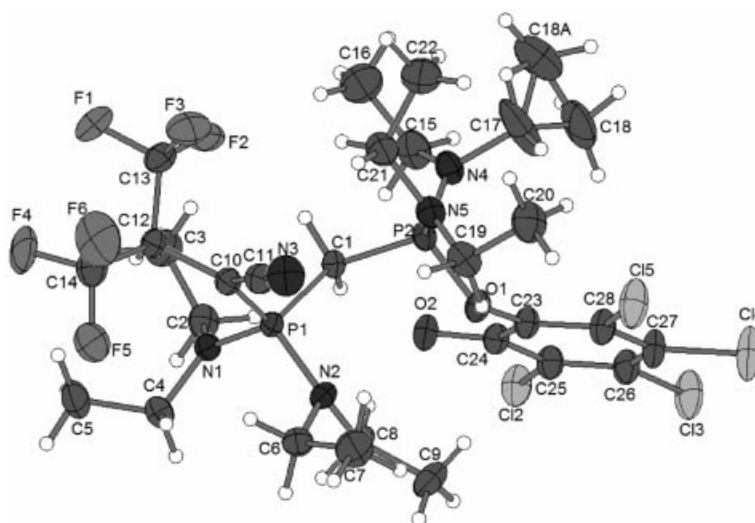
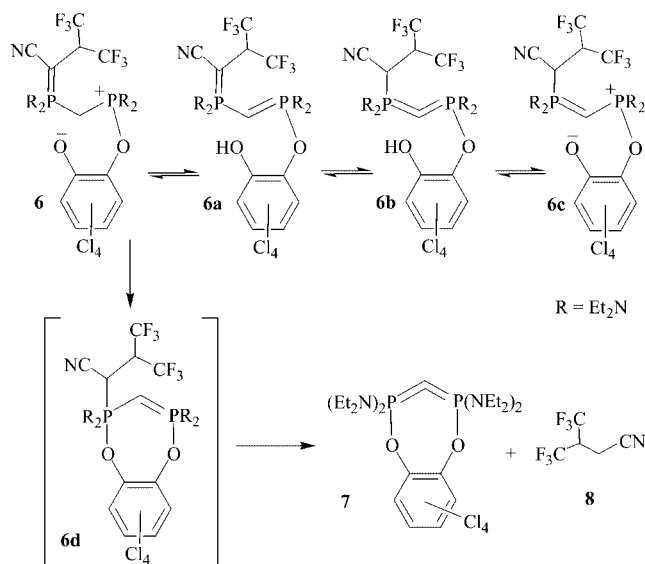


Figure 1. Perspective view and labeling scheme for **6**. Selected interatomic distances [pm] and bond angles [°]: P(1)–C(10) 171.4(3), P(1)–C(1) 183.0(3), C(1)–P(2) 179.5(2), P(1)–N(1) 165.3(2), P(1)–N(2) 165.5(2), P(2)–N(4) 161.2(2), P(2)–N(5) 162.3(2), C(10)–C(11) 139.7(4), C(11)–N(3) 116.1(4), C(10)–C(12) 151.3(3), P(2)–O(1) 157.93(19), O(2)–P(1) 415.9, O(2)–P(2) 320.1; C(10)–P(1)–C(1) 115.05(12), P(2)–C(1)–P(1) 122.90(14), C(11)–C(10)–C(12) 118.6(2), C(11)–C(10)–P(1) 122.0(2), C(12)–C(10)–P(1) 119.37(19), N(3)–C(11)–C(10) 178.8(3), O(1)–P(2)–C(1) 107.57(11), N(4)–P(2)–C(1) 106.08(12).



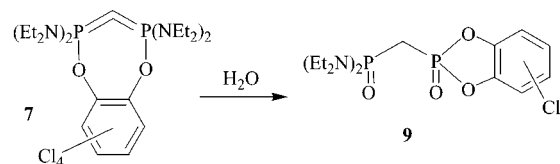
It is interesting that the ^{31}P NMR spectrum does not reflect all these changes of the molecule and shows two well-resolved doublets with constant chemical shifts at all temperatures below 20 °C.

In crystalline form zwitterion **6** is stable at room temperature under an inert atmosphere. For example, after 12 h we did not find additional signals in the NMR spectra. In chloroform solution compound **6** is stable up to 15 °C, and at 20 °C irreversible decomposition begins. The two doublets of **6** in the ^{31}P NMR spectrum become broad and unresolved and a new, sharp singlet appears at $\delta = 56.8$ ppm. After about 25–30 h the spectrum contains only traces of the starting material. The conversion of two doublets due to the two inequivalent phosphorus nuclei into one singlet, and its chemical shift value, indicate that compound **6** rearranges into the symmetrical carbodiphosphorane **7**, which contains magnetically equivalent phosphorus nuclei. In the ^{19}F NMR spectrum the decomposition of **6** is shown by the disappearance of the doublet at $\delta = -66.42$ ppm ($^3J_{\text{H,F}} = 8$ Hz) and the growth of a new doublet at $\delta = -68.04$ ppm ($^3J_{\text{H,F}} = 6.5$ Hz), which belongs to six equivalent fluorine atoms of the second decomposition product [hexafluoroisovaleronitrile (**8**)]. This compound is a colorless, volatile liquid that can be easily distilled from the reaction mixture together with the solvent (chloroform). Its structure was confirmed by NMR spectroscopy and mass spectrometry. The decomposition rate depends on the properties of the solvent used. In chlorobenzene it is twice as fast as in chloroform.

Unlike other known unstable zwitterions of this type, the negatively charged oxygen atom O(2) of the former orthoquinone unit does not form the expected 1,3,2-dioxaphospholane cycle with phosphorus P(2), but attacks the other positively charged phosphorus P(1). The mechanism of the decomposition should include the dissociation of the P(1)–C(10) ylidic bond and the elimination of two hydrogen atoms from the methylene unit. There is no clue as to whether these processes proceed consecutively or are con-

certed. Taking into account our previous results,^[1,2] as well as the recently reported P=C bond dissociation of strained four-membered cyclic ylides,^[9] the homolytic cleavage of the P(1)–C(10) ylidic bond of **6** with the intermediate formation of the reactive carbene in this reaction cannot be excluded. Another possible mechanism of the decomposition of **6** may include, for example, an intermediate formation of compound **6d** which, because of steric hindrance around phosphorus P(1), may eliminate **8** to give carbodiphosphorane **7**.

In the early stages of the decomposition of zwitterion **6** carbodiphosphorane **7** is the only product and no other signals except for those of the starting material and the product are observed in the ^{31}P and ^{19}F NMR spectra. However, after completion of the process the content of numerous by-products in the ^{31}P NMR spectrum reaches 30–40%. Carbodiphosphorane **7** is rather stable in the reaction solution and its signal decreases only gradually on heating to 70 °C during 10 h. However, our attempts to isolate the product in crystalline form failed. The structure of **7** was confirmed by its reaction with water. This process includes the formation of several intermediate compounds which finally give the product **9**. Unlike carbodiphosphorane **7**, this compound is not symmetrical and contains two magnetically inequivalent phosphorus atoms that appear as two doublets of an AB spin system at $\delta = 18.00$ and 30.72 ppm ($^2J_{\text{P,P}} = 5.5$ Hz) in the ^{31}P NMR spectrum. The signal at $\delta = 18$ ppm, when recorded without proton decoupling, appears as a characteristic doublet of triplets. It belongs to the phosphorus atom of the 1,3,2-dioxaphospholane system because of the interaction with only two P–CH₂–P protons. Compound **9** was isolated as colorless crystals and its structure was additionally confirmed by ^1H NMR and HR mass spectrometry.



Experimental Section

General Remarks: All operations were performed under nitrogen in a dry box. The solvents were dried by the usual procedures. The NMR spectra were recorded with Varian Gemini-400 and JEOL FX-90Q spectrometers. The ^1H and ^{13}C chemical shifts were referenced to tetramethylsilane (TMS). The ^{19}F and ^{31}P chemical shifts were measured using CFCl_3 and 85% aqueous H_3PO_4 as standards, respectively. The digital resolutions were 0.25, 0.5, 1.0, and 1.25 Hz for ^1H , ^{13}C , ^{19}F , and ^{31}P NMR spectra, respectively.

Zwitterionic Compound 6: A solution of tetrachloroorthobenzoquinone (37 mg, 0.150 mmol) in 2 mL of dry diethyl ether was added in portions of 5–8 drops to a solution of compound **3** (85 mg, 0.153 mmol) in 3 mL of diethyl ether at –10 °C. Each portion of TOB was added at an interval of 2–3 min. The reaction solution was left for 12 h at –10 °C and then for 48 h at –30 °C. The colorless crystals of **6** formed over this time were separated from the

mother liquor, washed with cold diethyl ether, and dried in vacuo (0.05 Torr). Yield: 73 mg (59%). ^1H NMR (CDCl_3 , 15 °C): δ = 1.12 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 12 H, NCH_2CH_3), 1.13 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 12 H, NCH_2CH_3), 2.62 (dd, $^2J_{\text{P,H}} = 16.5$, $^2J_{\text{P,H}} = 21.1$ Hz, 1 H, P-CH-P), 3.02–3.29 (m, 16 H, NCH_2CH_3), 3.47 [sept, $^3J_{\text{F,H}} = 6.9$ Hz, 1 H, $\text{CH}(\text{CF}_3)_2$], 4.74 (br. dd, $^2J_{\text{P,H}} = 18.4$, $^2J_{\text{P,H}} = 21.8$ Hz, 1 H, P-CH₂-P) ppm. ^{19}F NMR (CDCl_3): δ = –66.4 ppm (d, $^3J_{\text{H,F}} = 7.5$ Hz, 6 F). ^{31}P NMR (CDCl_3): δ = 44.5 (d, $^2J_{\text{P,P}} = 11.2$ Hz), 57.0 ppm (d, $^2J_{\text{P,P}} = 11.2$ Hz).

Decomposition of 6: A solution of freshly crystallized zwitterionic compound **6** in CDCl_3 was left at 20 °C for 24 h.

Carbodiphosphorane 7: ^{31}P NMR (CDCl_3): δ = 56.8 ppm (s).

Hexafluoroisovaleronitrile 8: ^1H NMR (CDCl_3): δ = 2.93 (d, $^3J_{\text{H,H}} = 6.5$ Hz, 2 H, CH_2CN), 3.37 ppm [m, $^3J_{\text{H,H}} = 6.5$, $^3J_{\text{F,H}} = 7.0$ Hz, 1 H, $(\text{CF}_3)_2\text{CH}$]. ^{19}F NMR (CDCl_3): δ = –68.0 ppm (d, $^3J_{\text{H,F}} = 7.0$ Hz, 6 F). MS (EI, 70 eV, 250 °C): m/z (%) 191 (2) [M^+], 172 (36) [$\text{M} - \text{F}$] $^+$, 122 (100) [$\text{M} - \text{CF}_3$] $^+$. HRMS [$\text{M} - \text{F}$]: calcd. 172.01857; found 172.01787 (–4.0 ppm, –0.7 mmu).

Compound 9: A solution of **6** (100 mg, 0.18 mmol) in CH_2Cl_2 (2 mL) was left at 20 °C for 24 h, then water (50 mg) was added and the mixture was stirred for 48 h at 20 °C. The solvent was evaporated, the residue was dried in vacuo (0.05 Torr), washed with diethyl ether and crystallized from toluene/hexane (at –20 °C) to give 15 mg of a colorless solid. ^1H NMR (CDCl_3): δ = 1.09 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 12 H, NCH_2CH_3), 2.40 (dd, $^2J_{\text{P,H}} = 16.5$, $^2J_{\text{P,H}} = 20.8$ Hz, 2 H, P-CH₂-P), 3.04 (m, 8 H, NCH_2CH_3) ppm. ^{31}P NMR (CDCl_3): δ = 18.0 (d, $^2J_{\text{P,P}} = 5.6$ Hz), 30.7 (d, $^2J_{\text{P,P}} = 5.6$ Hz) ppm. MS (CI, negative, NH_3 , 200 °C): m/z (%) 496 (90) [M]; (EI, 70 eV, 207 °C): m/z (%) 496 (10) [M^+], 424 (35) [$\text{M} - \text{Et}_2\text{N}$] $^+$. HRMS [M^+]: calcd. 495.98090; found 495.97677 (–8.3 ppm, –4.1 mmu); calcd. for [$\text{M} - \text{Et}_2\text{N}$]: 423.89957; found 423.89897 (–1.4 ppm, –0.6 mmu).

X-ray Crystallographic Study: The single-crystal X-ray structure determination was performed at 173(2) K on a Siemens P4 diffractometer using graphite-monochromated Mo- K_α radiation (λ = 71.073 pm) and an LT2 low temperature device. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program system.^[10]

Crystal data for **6** ($\text{C}_{28}\text{H}_{43}\text{Cl}_4\text{F}_6\text{N}_5\text{O}_2\text{P}_2$): M_w = 799.46, triclinic, space group $P\bar{1}$, a = 1199.2(2), b = 1279.93(15), c = 1428.87(17) pm, α = 82.875(8)°, β = 89.202(12)°, γ = 85.148(11)°, V = 2.1685(6) nm³, Z = 2, D_c = 1.484 Mg m^{–3}, μ = 0.654 mm^{–1}; 11563 reflections collected, 256 parameters refined using 9956 unique reflections (R_{int} = 0.0334) to final indices R_1 [$I > 2\sigma(I)$] =

0.0745 and wR_2 (all data) = 0.1465 [$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + P]$], where $P = (2F_o^2 + F_c^2)/3$. All non-hydrogen atoms were refined anisotropically and the position of the hydrogen atoms was calculated as a riding model. The final residual Fourier positive and negative peaks were equal to 1.024 and –1.034 e Å^{–3}. One ethyl group of one NEt_2 moiety is disordered. The terminal C(18) atom is split over two positions with an occupancy of 70% for C(18) and 30% for C(18a). The distances C(17)–C(18) and C(17)–C(18a) were set to be equal. The Cl atoms of one solvent molecule are disordered over two positions (50% occupancy). The distances C(30)–Cl(8), C(30)–Cl(9), C(30)–Cl(8a) and C(30)–Cl(9a) were set to be equal.

CCDC-610625 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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