

The Surprisingly Facile Dehydrohalogenation of a Hydrazonoyl Chloride into a Stable Phosphorus-substituted Nitrilimine

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Tetrachloro-*o*-benzoquinone reacts with bis(diisopropylamino)thioxophosphoranenitrile *N*-[(phenyl)(2,4,6-trifluoromethylphenyl)phosphanyl]imide **1b** affording the corresponding $\sigma^{5\lambda,5}$ -phosphorus-substituted nitrilimine **2b**; addition of HCl to **2b** leads to hydrazonoyl chloride **4b** which gives back nitrilimine **2b** by simple filtration on silica gel.

A huge variety of hydrazonoyl halides have been described in journals and the patent literature, mainly because of their pesticidal activity.¹ Some of them have been tested as nitrilimine precursors.² Dehydrohalogenations were effected by base; an equilibrium was believed to be established, lying

far on the side of the reactants, and thus nitrilimines were formed in low concentration and trapped.³ Here we report the easy and quantitative conversion of a hydrazonoyl chloride into a stable nitrilimine which is, in fact, the first example of an isolated $\sigma^{5\lambda,5}$ -phosphorus substituted nitrilimine.

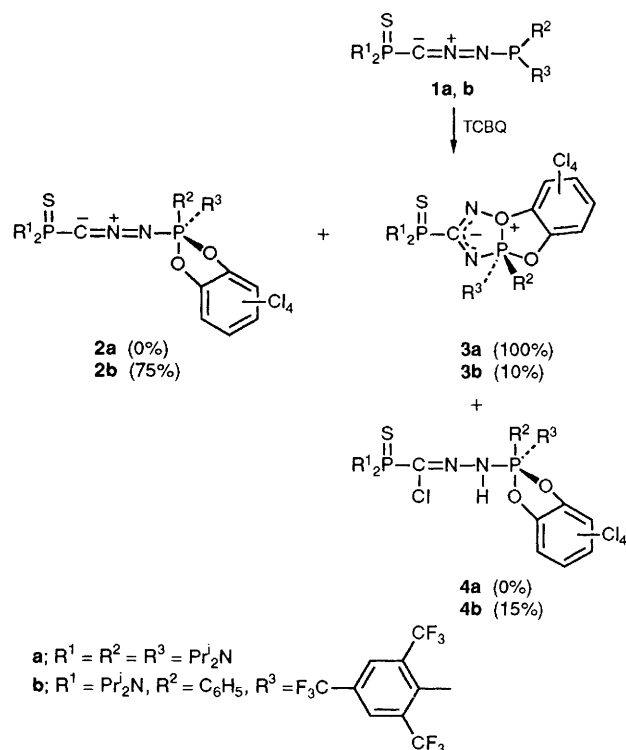
Recently we reported that the reaction of nitrilimine **1a**,^{4a,b} bearing diisopropylamino groups at both phosphorus atoms, with tetrachloro-*o*-benzoquinone (TCBQ) gave rise to a 'nitrene-oxygen complex' **3a** and not to the corresponding five-coordinated phosphorus substituted nitrilimine **2a** (Scheme 1).⁵ In the hope of obtaining such a compound, we have started a systematic study on the role of the phosphorus substituents. According to ³¹P NMR spectroscopy, when a stoichiometric amount of TCBQ was added to a tetrahydrofuran (THF) solution of nitrilimine **1b**, at -20 °C, a mixture of three products **2b-4b** was formed in a 75 : 10 : 15 ratio. One of the minor products was isolated, as an air-stable white solid (8% yield), after evaporation and several washings of the residue with acetonitrile, and spectroscopically characterized as the hydrazoneyl chloride **4b**.[†] On the other hand separation of the crude reaction mixture by column chromatography led to the nitrilimine **2b** and 'nitrene-oxygen complex' **3b** as white solids in 50 and 5% yield, respectively.[†] The structure of **3b** was deduced by comparing its physical data[†] with those of the analogous compound **3a**.⁵ Nitrilimine **2b** presented a typical (i) IR absorption at 2162 cm⁻¹ (ν CNN);⁴ (ii) ¹³C NMR doublet at δ 65.53 (CNN, *J*_{PC} 133.7 Hz);⁴ (iii) ³¹P NMR doublet at δ 27.82 (λ⁵σ⁴P, *J*_{PP} 8.6 Hz).^{4a-c} The phosphorane nature of the second phosphorus atom was obvious from the high field ³¹P NMR chemical shift (δ -24.35).⁶

In contrast to most nitrilimines,^{2,4} **2b** does not react with classical dipolarophiles to give 2 + 3 cycloadducts. However, it readily reacts *via* a 1,3 addition process, at room temperature. With amines, including bulky ones, such as diisopropylamine, hydrazone **5** was obtained in fair yield.

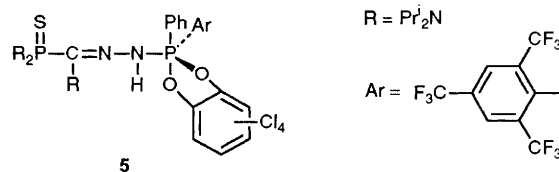
Addition of ethereal hydrogen chloride to **2b** gave rise to hydrazoneyl chloride **4b** in quantitative yield. The formation, in low yield, of this product in the reaction of TCBQ with nitrilimine **1b** is thus simply due to the presence of a small amount of HCl, in the commercially available quinone, which adds to the primary formed nitrilimine **2b**. Surprisingly, elimination of hydrogen chloride occurs during the filtration of an ethereal solution of **4b** on silica gel, quantitatively giving back nitrilimine **2b** [eqn. (1)]. Note that, during this treatment, no hydrolysis can be detected which is surprising for both nitrilimine and phosphorane moieties.



[†] Selected data for **2b**, **3b**, **4b** and **5**. All compounds gave satisfactory elemental analyses. **2b**, m.p. 166–167 °C; ¹H NMR (CDCl₃) δ 1.26 (d, *J*_{HH} 6.8 Hz, 6 H, CH₃CHN), 1.38 (d, *J*_{HH} 6.8 Hz, 6 H, CH₃CHN), 1.40 (d, *J*_{HH} 6.8 Hz, 6 H, CH₃CHN), 1.41 (d, *J*_{HH} 6.8 Hz, 6 H, CH₃CHN), 3.74 (sept d, *J*_{PH} 20.7 Hz, *J*_{HH} 6.8 Hz, 2 H, CH₃CHN), 3.75 (sept d, *J*_{PH} 20.7 Hz, *J*_{HH} 6.8 Hz, 2 H, CH₃CHN), 7.37–7.80 (m, 5 H, C₆H₅) and 8.07 [d, *J*_{PH} 3.7 Hz, 2 H, (CF₃)₃C₆H₂]; ¹³C NMR (CDCl₃) δ 22.13 (d, *J*_{PC} 2.2 Hz, CH₃CHN), 22.42 (d, *J*_{PC} 2.6 Hz, CH₃CHN), 22.75 (s, CH₃CHN), 46.88 (d, *J*_{PC} 5.8 Hz, CH₃CHN), 47.28 (d, *J*_{PC} 5.6 Hz, CH₃CHN) and 65.53 (d, *J*_{PC} 133.7 Hz, C=N); **3b**, m.p. 268–269 °C; ³¹P NMR (THF) δ +48.36 and -32.07 (*J*_{PP} 5.1 Hz); ¹³C NMR (CDCl₃) δ 22.22 (d, *J*_{PC} 6.5 Hz, CH₃CHN), 22.29 (s, CH₃CHN), 22.80 (d, *J*_{PC} 2.5 Hz, CH₃CHN), 24.01 (s, CH₃CHN), 48.00 (d, *J*_{PC} 5.4 Hz, CH₃CHN), 48.93 (d, *J*_{PC} 5.5 Hz, CH₃CHN) and 155.40 (d, *J*_{PC} 177.8 Hz, C=N); **4b**, m.p. 169 °C; ³¹P NMR (THF) δ +61.03 and -22.85 (*J*_{PP} 4.7 Hz); ¹H NMR (CDCl₃) δ 7.71 (d, *J*_{PH} 28.9 Hz, 1 H, NH); ¹³C NMR (CDCl₃) δ 23.17 (d, *J*_{PC} 2.1 Hz, CH₃CHN), 23.43 (d, *J*_{PC} 2.7 Hz, CH₃CHN), 23.78 (d, *J*_{PC} 3.0 Hz, CH₃CHN), 24.02 (d, *J*_{PC} 4.1 Hz, CH₃CHN), 47.65 (d, *J*_{PC} 5.3 Hz, CH₃CHN) and 147.19 (d, *J*_{PC} 137.1 Hz, C=N); IR (KBr) ν_{max} 3305 cm⁻¹ (NH); **5**, pale yellow oil, *R*_f 0.8 (hexane-diethyl ether, 70 : 30); ³¹P NMR (CDCl₃) δ +69.08 and -32.25 (*J*_{PP} 7.3 Hz); ¹H NMR (CDCl₃) δ 8.36 (d, *J*_{PH} 44.1 Hz, 1 H, NH); ¹³C NMR (CDCl₃) δ 19.47, 21.48 (s, CH₃CHNC), 23.33 (d, *J*_{PC} 4.5 Hz, CH₃CHNP), 24.27 (s, CH₃CHNP), 24.66 (d, *J*_{PC} 4.2 Hz, CH₃CHNP), 24.92 (d, *J*_{PC} 4.0 Hz, CH₃CHNP), 25.27, 25.36 (s, CH₃CHNC), 46.71 (d, *J*_{PC} 6.1 Hz, CH₃CHNP), 47.01 (d, *J*_{PC} 5.2 Hz, CH₃CHNP), 48.88, 49.73 (s, CH₃CHNC) and 152.48 (dd, *J*_{PC} 162.7 and 14.5 Hz, C=N).



Scheme 1 The percentages in parentheses refer to the product distribution as determined by ³¹P NMR spectroscopy



In order to understand the easy elimination of HCl, an X-ray crystal structure determination was performed on hydrazoneyl chloride **4b**,[‡] and a portion of its molecular structure is shown in Fig. 1 along with the atom numbering scheme and the pertinent metric parameters. The basic structural features, for the five-coordinated phosphorus atom, conform closely to a square pyramid with the phenyl group [C(7)] located at the apical site; the average axial-basal and *cis*-basal angles are 102.4 and 86.6°, respectively (the corresponding values for an idealized square pyramid are 105 and 86°).⁷ The least-squares plane for the four basal atoms [O(1), O(2), C(13), N(1)] shows small average out-of-plane variations (0.014 Å). Note that this square-pyramidal geometry is unusual for a monocyclic phosphorane.⁸ Of special interest, the value of the N(1)N(2)C(22)P(2) dihedral angle [176.9 (2)°] is close to that observed for known nitrilimines,⁴ and the Cl(5) and H(N1) are only -0.0319(9) and 0.279(2) Å out of the N(1)N(2)C(22) plane. This geometry combined with the fact that the H(N_A) and Cl(5) are only 2.45 Å apart, could explain the facile elimination of HCl from **4b**.

[‡] Crystal data for compound **4b**: C₃₄H₃₆Cl₅F₉N₄O₂P₂S, *M* = 974.95, triclinic, space group *P*1, *a* = 11.978(2), *b* = 16.641(2), *c* = 11.710(2) Å, α = 108.88(1), β = 104.82(2), γ = 76.33(1)°, *V* = 2105(1) Å³, *Z* = 2, *D*_c = 1.54 g cm⁻³, μ = 5.4 cm⁻¹. Measurements: CAD4, radiation: Mo-Kα (λ = 0.71073 Å); solution: direct methods. 6963 unique reflections, 5092 observed [*F*_o² > 3σ(*F*_o²)], number of variable: 541 (all non-H atoms anisotropic). *R* = 0.031, *R*_w = 0.032. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

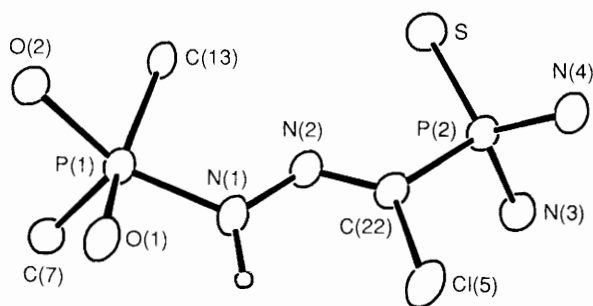


Fig. 1 Simplified ORTEP diagram of **4b**, showing 40% probability ellipsoids. Some metric data include: P(1)–O(1) 1.748(2); P(1)–O(2) 1.706(2); P(1)–C(7) 1.794(3); P(1)–C(13) 1.913(3); P(1)–N(1) 1.701(3); N(1)–N(2) 1.354(4); N(2)–C(22) 1.258(4); C(22)–P(2) 1.854(4); C(22)–Cl(5) 1.768(3) Å; N(1)–P(1)–O(1) 81.6(1); N(1)–P(1)–O(2) 149.4(1); N(1)–P(1)–C(7) 110.5(1); N(1)–P(1)–C(13) 93.2(1); O(1)–P(1)–O(2) 88.0(1); O(1)–P(1)–C(7) 96.8(1); O(1)–P(1)–C(13) 153.5(1); O(2)–P(1)–C(7) 99.2(1); O(2)–P(1)–C(13) 83.5(1); C(7)–P(1)–C(13) 103.4(1); P(1)–N(1)–N(2) 120.9(2); P(1)–N(1)–H 119.6; N(2)–N(1)–H 119.6; N(1)–N(2)–C(22) 120.4(2); N(2)–C(22)–Cl(5) 120.6(3); N(2)–C(22)–P(2) 119.4(2); Cl(5)–C(22)–P(2) 120.0(2)°.

All attempts to rearrange nitrilimine **2b** into compound **3b** failed, strongly suggesting that this is not the intermediate in the formation of the 'nitrene–oxygen complex.' Further studies are now under way to elucidate the mechanism leading to **3b**.

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