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The Abnormal Hydrolysis of 7-Phosphanorbornenium Salts: A Case of Phosphonium−Phosphenium Equivalence

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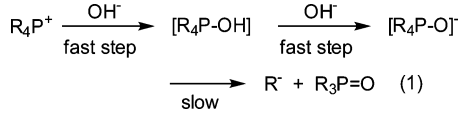
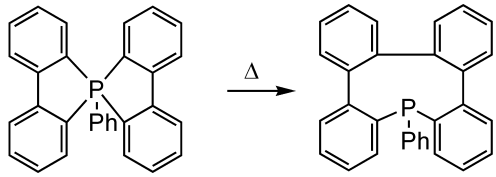
Phosphonium salt hydrolysis is certainly one of the most fundamental and well-studied reactions in organophosphorus chemistry.[1] The accepted mechanism is schematized in eq 1.

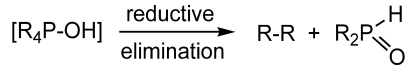
When Wittig discovered pentaarylphosphoranes, he also showed



that when phosphorus is incorporated in a five-membered ring, one of the favored decomposition pathways involves a reductive elimination, as shown in eq 2.[2] On this basis, it seemed quite

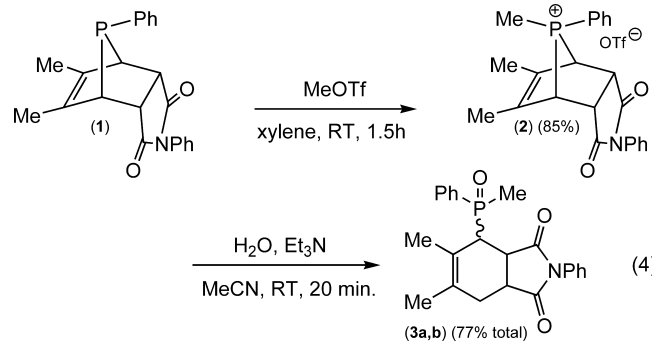


possible to alter the normal course of a phosphonium salt hydrolysis to get a phosphinous acid[3] instead of the classical phosphine oxide (eq 3). In such a case, the phosphonium salt would become

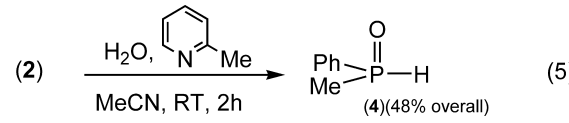


synthetically equivalent to a phosphenium ion, whose chemistry is only modestly developed at the present time.[4] In order to realize this possibility, it would suffice to find a system in which the reductive elimination occurs faster than the normally slow release of the R^- carbanion. A structure of choice in this regard is the 7-phosphanorbornene bicyclic system. Indeed, following extensive studies by Quin[5] and us,[6] it has been shown to readily lose its phosphorus bridge under a variety of conditions through retro-McCormack reactions. Here we report that it is possible to direct the hydrolysis of phosphanorbornenium salts toward either the normal or abnormal pathway by just slightly manipulating the experimental parameters.

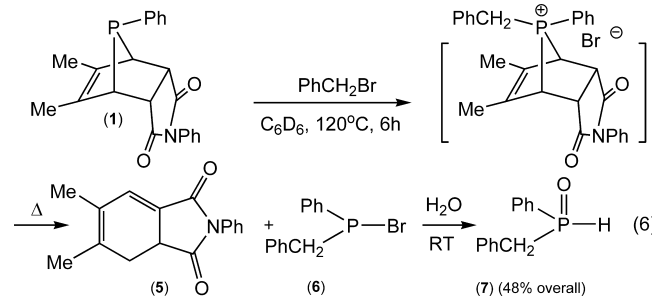
The quaternization of (**1**)[6a] by methyl triflate is complete at room temperature in 1.5 h. The salt (**2**)[7] is insoluble in most organic solvents, as expected for an ionic compound. It does not react with neutral water but is rapidly hydrolyzed in the presence of triethylamine to give the expected product as a mixture of two isomers (**3a,b**)[8] (eq 4). Quite strikingly, when triethylamine is replaced by α-picoline, the reaction pathway changes completely, and the sole



product of the reaction is the secondary phosphine oxide (**4**)[9] resulting from cleavage of the phosphorus bridge (eq 5).



In a preceding paper, we demonstrated that 7-R-7-phosphanorbornenes can be considered as synthetic equivalents of nucleophilic phosphinidenes [RP] on the basis of their transformation into phosphinites by quaternization and alcoholysis in the presence of triethylamine.[6c] The intermediate phosphoniums were not characterized. The result of eq 4 seemed to contradict our preceding results. Thus, we decided to monitor by NMR the reaction of (**1**) with benzyl bromide in C_6D_6. At 120 °C, the phosphonium collapses to give the bromophosphine (eq 6).[10]



In order to rationalize these experimental findings, we decided to perform density functional theory calculations at the B3LYP/6-311+G(d,p) level[11] on the model compounds (**8**)−(**10**) (eq 7). The computed structures of (**8**) and (**9**) are shown in Figure (1). The structure of (**8**) shows that it is an ion pair with a P−Br separation of 2.85 Å (P−Br 2.22 Å in PBr_3).[12] Instead of being in the plane of symmetry of the phosphanorbornene cation, the two Me groups on P are displaced away from the Br atom as a result of this

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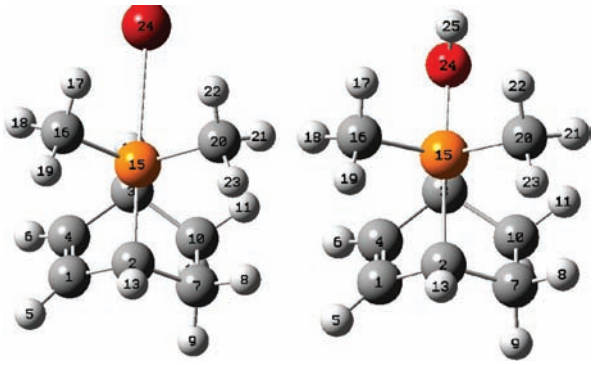
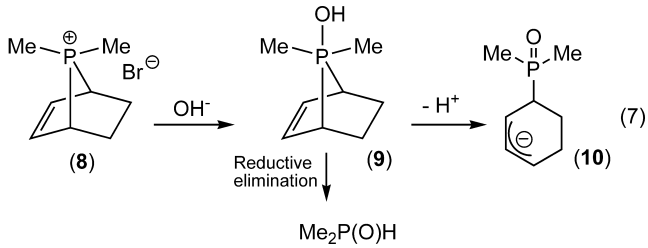


Figure 1. Computed structures of (**8**) and (**9**). Most significant bond lengths (Å) and angles (deg) for (**8**): P−Br, 2.848; P−C2, 1.911; P−C3, 1.888; P−C15, 1.828; P−C20, 1.832; C2−P−C3, 79.6; Br−P−C15, 84.6; Br−P−C20, 83.3; C15−P−C20, 112.6. For (**9**): P−O, 1.783; P−C2, 2.02; P−C3, 1.924; P−C15, 1.844; P−C20, 1.855; C2−P−C3, 76.3; O−P−C15, 94.0; O−P−C20, 92.3; C15−P−C20, 110.0.



interaction. The strain of the bridge and the long P−C bridge bonds explain why (**8**) can collapse easily to give the dimethylbromophosphine. The calculations show that (**9**) is a genuine intermediate (a local minimum with no imaginary frequencies). Its structure displays very long P−C bridge bonds, even longer than the corresponding bonds in (**8**). The bridge is very strained, with a C−P−C angle of 76.3°, which is smaller than the corresponding angle in (**8**). These data suggest that (**9**) loses its bridge very easily. Upon removal of the hydroxyl proton from (**9**), the bicyclic structure directly collapses to give (**10**) with no detectable intermediate or transition state. On this basis, we explain our results as follows. When the hydrolysis of (**2**) is conducted in weakly basic media,[13] the half-life of the intermediate hydroxyphosphorane is sufficiently long that this species can lose its bridge to give the phosphinous acid. When the hydrolysis is conducted in strongly basic media, the fast deprotonation induces the collapse toward the tertiary phosphine oxide.

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Supporting Information Available: Complete ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) (**2**): ^{31}P NMR (DMSO-d_6): δ 83.7. ^{1}H NMR (DMSO-d_6): δ 1.88 (s, 6H, Me−C), 2.31 (d, J_{HP} = 14.4 Hz, Me−P), 3.69 (d, 2H, J_{HH} = 1.2 Hz, CH−CO), 4.37 (dd, 2H, J_{HP} = 5.4, CH−P), 7.03 (m, 2H, NPh), 7.45−7.53 (m, 3H, NPh), 7.73−7.86 (m, 3H, PPh), 8.08−8.15 (m, 2H, PPh). ^{13}C NMR (DMSO-d_6): δ 4.44 (d, J_{CP} = 51.7 Hz, Me−P), 15.40 (Me−C), 44.34 (d, J_{CP} = 16.3 Hz, CH(CO)), 45.40 (d, J_{CP} = 55.1 Hz, CH−P), 119.30 (d, J_{CP} = 41.5 Hz, C *ipso* Ph−P), 174.03 (d, J_{CP} = 15.5 Hz, CO).

(8) (**3a**,**b**) was separated by chromatography on silica gel with 20:1 CH_2Cl_2/EtOH as the eluent. (**3a**): first eluted, yield 39.2% from (**2**). ^{31}P NMR ($CDCl_3$): δ 41. ^{1}H NMR ($CDCl_3$): δ 1.75 (d, J_{HP} = 12.9 Hz, Me−P), 1.84 (d, J_{HP} = 5.1 Hz, Me−C), 1.89 (s, Me−C), 2.48 (d, 1H, J_{HH} = 15.3 Hz, CH_2), 3.21−3.44 (m, 4H, CH + CH_2), 7.13−7.16 (m, 2H, NPh), 7.35−7.44 (m, 3H, PPh), 7.56 (br, 3H, NPh), 7.80−7.83 (m, 2H, PPh). ^{13}C NMR ($CDCl_3$): δ 15.92 (d, J_{CP} = 69.3 Hz, Me−P), 20.55 (d, J_{CP} = 3.1 Hz, Me−(C)), 21.23 (d, J_{CP} = 2.3 Hz, Me−(C)), 31.61 (d, J_{CP} = 2.8 Hz, CH_2), 39.73 (d, J_{CP} = 2.9 Hz, CH), 40.65 (s, CH), 46.28 (d, J_{CP} = 69.4 Hz, CH−P), 121.15 (d, J_{CP} = 7.4 Hz, C *ipso* NPh), 126.18 (s, CH NPh), 128.57 (s, CH *para* NPh), 129.05 (d, J_{CP} = 11.1 Hz, CH PPh), 129.06 (s, CH NPh), 130.46 (d, J_{CP} = 8.8 Hz, CH PPh), 131.95 (s, C(Me)), 132.13 (d, J_{CP} = 2.7 Hz, C(Me)), 132.59 (d, J_{CP} = 91.3 Hz, C *ipso* PPh), 133.49 (d, J_{CP} = 8.7 Hz, CH *para* PPh). (**3b**): yield 36.4%. ^{31}P NMR ($CDCl_3$): δ 38. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, Me−C), 1.61 (d, J_{HP} = 5.1 Hz, Me−C), 1.91 (d, J_{HP} = 12 Hz, Me−P), 2.26 (d, 1H, J_{HH} = 15.9 Hz, CH_2), 2.72 (br, 1H, CH_2), 3.18 (d, J_{HP} = 10.5 Hz, CH−P), 3.40 (m, CH), 3.80 (m, CH), 7.18 (m, 2H, NPh), 7.34−7.60 (m, 6H, NPh + PPh), 7.68−7.74 (m, 2H, PPh). ^{13}C NMR ($CDCl_3$): δ 15.47 (d, J_{CP} = 66.9 Hz, Me−P), 20.16 (d, J_{CP} = 3.0 Hz, Me−(C)), 20.32 (d, J_{CP} = 1.7 Hz, Me−(C)), 31.12 (d, J_{CP} = 2.6 Hz, CH_2), 39.55 (d, J_{CP} = 2.9 Hz, CH), 40.66 (s, CH), 47.39 (d, J_{CP} = 68.9 Hz, CH−P), 121.61 (d, J_{CP} = 7.4 Hz, C *ipso* NPh), 126.25 (s, CH NPh), 128.57 (d, J_{CP} = 10.8 Hz, CH PPh), 128.64 (s, CH *para* NPh), 129.11 (s, CH NPh), 130.61 (d, J_{CP} = 8.9 Hz, CH PPh), 131.97 (s, C(Me)), 132.19 (d, J_{CP} = 2.6 Hz, C(Me)), 132.07 (d, J_{CP} = 95.6 Hz, C *ipso* PPh), 132.29 (d, J_{CP} = 9.3 Hz, CH *para* PPh).

(9) (**4**): purified by chromatography with EtOAc/CH_2Cl_2 as the eluent, yield 48% from (**1**). ^{31}P NMR ($CDCl_3$): δ 20.6 (d, J_{PH} = 474 Hz). ^{1}H NMR ($CDCl_3$): δ 1.71 (dd, 3H, $^{3}J_{HH}$ = 3.9 Hz, J_{HP} = 13.8 Hz, Me), 7.43−7.50 (m, 3H, Ph), 7.54 (dq, J_{HP} = 475 Hz, $^{3}J_{HH}$ = 3.9 Hz, PH), 7.60−7.67 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 16.25 (d, J_{CP} = 68.8 Hz, Me), 128.89 (d, J_{CP} = 12.6 Hz, CH Ph), 129.49 (d, J_{CP} = 11.2 Hz, CH Ph), 131.97 (d, J_{CP} = 99.7 Hz, C *ipso* Ph), 132.42 (s, C *para* Ph).

(10) (**5**): ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, Me), 1.94 (s, 3H, Me), 2.36−2.47 (m, 1H, CH_2), 2.61−2.70 (m, 1H, CH_2), 3.49−3.59 (m, 1H, CH), 6.90 (d, 1H, =CH), 7.34−7.50 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): 17.15 (s, Me), 20.06 (s, Me), 30.66 (s, CH_2), 38.59 (s, CH) 122.75, 126.41, 126.50, 128.34, 129.04, 132.07, 133.75, 136.89 (s, sp^2-C), 166.95 (s, CO), 175.30 (s, CO). MS: *m/z* 254.0 (100, $[M + H]^+$). (**6**): ^{31}P NMR (C_6D_6): δ 75.6. ^{1}H NMR (C_6D_6): δ 3.08 (d, J_{HP} = 7.3 Hz, CH_2). ^{13}C NMR (C_6D_6): δ 42.92 (d, J_{CP} = 33.6 Hz, CH_2). (**7**): yield 48% from (**1**). ^{31}P NMR ($CDCl_3$): δ 30 (d, J_{PH} = 475 Hz). ^{1}H NMR ($CDCl_3$): δ 3.34 (dt, 1H, $^{2}J_{HH}$ = J_{HP} = 14.6 Hz, CH_2), 3.46 (dt, 1H, $^{2}J_{HH}$ = J_{HP} = 14.6 Hz, CH_2), 7.05 (m, 2H, benzyl), 7.20−7.29 (m, 3H, benzyl), 7.40−7.55 (m, 5H, Ph), 7.46 (dt, J_{HP} = 475 Hz, $^{3}J_{HH}$ = 3.2 Hz, PH). ^{13}C NMR ($CDCl_3$): δ 38.76 (d, J_{CP} = 62.4 Hz, CH_2).

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