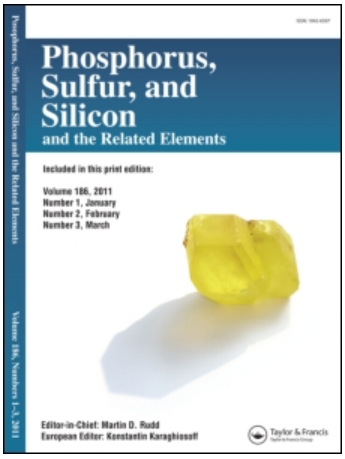

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PENTACOORDINATE SPIROCYCLIC DERIVATIVES OF THE 2H-1,2,3-DIAZAPHOSPHOLE SYSTEM

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Stable spirocyclic phosphoranes **2** have been prepared stereospecifically in high yields (90–95%) by reaction of *o*-azidophenol with *cis* and *trans*-diazaphosphole derivatives **1**. Slow isomerization of pure diastereoisomer **2** was observed in acidic conditions.

In the past few years considerable interest has been devoted to the synthesis of stable, isolable pentacoordinate phosphorus compounds;[1] in particular many attractive stereochemical results have been obtained in the field of spirophosphoranes[1] depending on the constraints of the two ring systems attached to the central atom.

In our previous papers, the synthesis[2] and chemical reactions[3] of some derivatives of the new 2H-1,2,3-diazaphosphole system have been reported. Now we wish to present the first examples of stable and isolable spirophosphorane derivatives of this system prepared by treatment of the *cis* and *trans* diazaphosphole derivatives **1** with *o*-azidophenol.[4]

Thus, addition of equimolar amounts of *o*-azidophenol to dry benzene solutions of diazaphospholes *cis*-**1**,[5] at room temperature, led to evolution of nitrogen with stereospecific formation of the corresponding spirophosphoranes *cis*-**2**. The reactions go to completion as shown by t.l.c. within *ca.* 20 h. Evaporation and crystallization or chromatography of the residue furnished spirophosphoranes *cis*-**2** in 90–95% yields.

Under the same conditions isomers *trans*-**1** led stereospecifically to spirophosphoranes *trans*-**2** (ca. 90%). Reaction as in the Scheme is assumed.

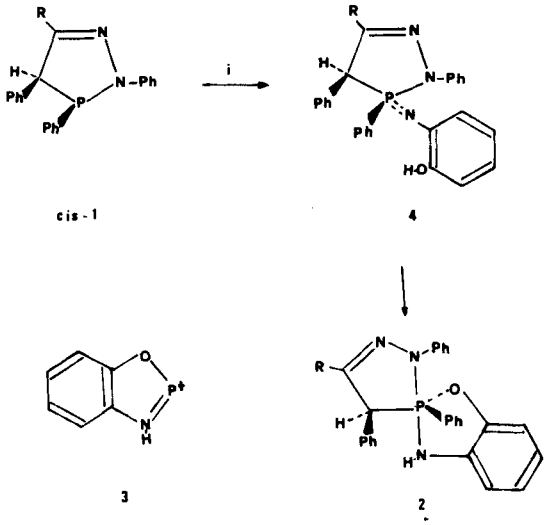
The reaction products **2** were identified on the basis of elemental analysis and spectral data (see Experimental Section). In particular the ir spectra showed the expected sharp NH stretching absorption at *ca.* 3440 cm^{-1}. The mass spectra showed, in addition to the parent ion, the base peak at m/e 138 most reasonably due to the phosphenium ion 3 ($C_6H_5NOP^+$); ^{31}P chemical shifts were found to fall upfield from an 85% H_3PO_4 reference clearly indicating[6] the pentacoordinate structure of **2**.

Structural assignment to *cis-trans* isomer **1** has been previously[5] made on the basis of ^1H n.m.r. spectroscopy; isomer assignment to *cis* and *trans* **2** was made on the same line: *i.e.* the *trans* configuration was assigned to the isomer showing an upfield methine signal and a much smaller J(PCH) value.

It should be noted that the benzylic protons in **2b** appeared as the AB portion of an ABX pattern (where X = ^{31}P), with δ_A 3.85 ppm, J_{AX} = 3 Hz, δ_B 3.57 ppm, $J_{BX} \leq 1$ Hz, J_{AB} = 15 Hz for *cis*-**2b** and δ_A 3.90 ppm, J_{AX} = 4 Hz, δ_B 3.42 ppm, J_{BX} < Hz, J_{AB} = 15 Hz for *trans*-**2b**.

The reactions were also studied in n.m.r. tubes in C_6D_6 solution and the doublet due the methine proton of the starting phosphine **1** was shown to be slowly replaced by the doublets due to the methine and NH protons of the corresponding spirocompound **2**. No absorption due to the intermediate phosphazene **4** was observed.

The assigned trigonal bipyramidal (TBP) structure **2** in the scheme is only tentative. In fact a square pyramidal geometry (SP) or "mixes" of the two structures[7] cannot be ruled out at present; although the difference in energy for the TBP and SP geometries may be very small, the extreme case with two (or three) electronegative and three (or two) electropositive ligands to phosphorus might be expected to lie nearer the TBP extreme. Moreover, although the oxygen would be expected to be apical in accord with its higher electronegativity, structure **2** with apical nitrogens would appear to be favoured by its stabilization due to ligand subset symmetry.[8]



(a, R = Ph; b = Ph-CH_2; i = *o*-azidophenol)
SCHEME 9

Spirophosphoranes **2** are very stable compounds which can be stored indefinitely at room temperature and are unchanged on treatment with a methanolic aqueous solution for several hours.

The good stability of spirophosphoranes **2** is reflected in their instantaneous formation from the precursor phosphazene **4** which could not be detected. However, during the acquisition of the ^{1}H n.m.r. data of *cis*-**2b** (or *trans*-**2b**) in $CDCl_3$ solution at room temperature a slow isomerization to *trans*-**2b** (or *cis*-**2b**) was observed, no evidence of isomerization being found for **2a** in the same solvent up to 80°C. Since *cis-trans*-**2b** appeared to be configurationally stable in C_6D_6 solution, some isomerization occurring also in CD_2Cl_2, we thought that the presence of trace amounts of HCl both in $CDCl_3$ and in CD_2Cl_2 might be responsible for the isomerization. Control experiments in fact showed that addition of very small amounts of hydrogen chloride to benzene solutions of pure *cis*- and *trans*-**2b** brought about an acceleration of their isomerization. Analogous behaviour was observed also with *cis-trans* phosphoranes **2a**. These findings provide clear evidence that trace amounts of hydrogen chloride can induce isomerization of these phosphoranes **2**; since no isomerization could be observed in all cases on heating benzene solutions of **2** up to 100°C in the absence of hydrogen chloride a pseudorotation mechanism would appear to be excluded. The mechanism of this process cannot be readily rationalized at present and further study is necessary.

In conclusion compounds **2** represent the first examples of isolable phosphoranes of the 2H-1,2,3-diazaphosphole system and these results support our suggestions that unstable pentacoordinate phosphorus compounds can be invoked as intermediates in previously reported[3a,b] reactions of some derivatives of this heterocyclic system. Moreover stereospecific formation of diastereomers **2** also implies stereospecific formation of the intermediate phosphazene **4**; on the other hand the ready availability of pure isomers **2** appears to be useful for the study of the stereochemistry of nucleophilic substitution of such spirophosphoranes *via* hexacoordinate intermediates.

EXPERIMENTAL

^{1}H n.m.r. spectra were obtained at 60 MHz for solutions in $CDCl_3$. ^{31}P n.m.r. spectra were obtained at 24.3 MHz for solutions in $CDCl_3$; chemical shifts upfield from external 85% H_3PO_4 are quoted as positive. Ir spectra are for $CHCl_3$ solutions. The micro-analyses were performed on pure isomers as well as on mixture of *cis-trans* isomers. The results obtained were practically identical. Melting points are uncorrected.

Preparation of Spirophosphoranes 2

o-Azidophenol (0.242 g, 2×10^{-3} mol) was added to a solution of the diazaphosphole *cis*-**1a** (0.784 g, 2×10^{-3} mol) in dry benzene (70 ml) and the resulting mixture was allowed to stand at room temperature until nitrogen evolution ceased (ca. 20 h). The course of the reaction was followed also by t.l.c. (SiO_2). Evaporation and crystallization of the residue from *n*-hexane gave phosphorane *cis*-**2a** as a white solid (95% yield), mp 190–192°C. The reaction product can be also purified by chromatography on a silica gel column, using as eluant a 15:1:1 *n*-hexane:ether:benzene mixture. Pure *cis*-**2a** (Rf 0.30) showed: I.r. ν_{max} 3440 (NH) cm^{-1}; ^{31}P + 33.0 ppm; ^{1}H n.m.r. δ 4.70 (d, 1H, J(P—H) 21 Hz, NH) 5.05 (d, 1H, J(P—H) 27 Hz, CH), 6.60–7.80 (m, 24H, ArH) ppm; MS m/e 499 (M^+), 138 (100%). (Found: C, 76.75: H, 5.21; N, 8.52; $C_{32}H_{26}N_3OP$ requires C, 76.94; H, 5.25; N, 8.41%).

In a similar way diazaphosphole *trans*-**1a** afforded phosphorane *trans*-**2a** (90%) (Rf 0.20, m.p. 183–185°C (from *n*-hexane), i.r. ν_{max} 3442 (NH) cm^{-1}, ^{31}P + 34.3 ppm; ^{1}H n.m.r. δ4.80 (d, 1H, J(P—H) 10 Hz, CH), 4.80 (d, 1H, J(P—H) 20 Hz, NH), 6.05–7.35 (m, 24H, ArH) ppm; MS m/e 499 (M^+), 138 (100%). (Found: C, 76.83; H, 5.27; N, 8.32%).

In an analogous fashion diazaphosphole *cis*-**1b** furnished the corresponding phosphorane *cis*-**2b** (94%) (Rf 0.25) mp 182–185°C (from *n*-pentane), i.r. ν_{max} 3340 (NH) cm^{-1}; ^{31}P + 35.2 ppm; ^{1}H n.m.r. δ3.50–3.80 (AB portion of an ABX pattern where X = ^{31}P, 2H, CH_2), 4.52 (d, 1H, J(P—H) 29 Hz, CH), 4.9 (d, 1H J(P—H) 21 Hz, NH), 6.40–7.93 (m, 24H, ArH); MS m/e 513 (M^+), 138 (100%). (Found: C, 77.23, H, 5.52, N, 8.15. $C_{33}H_{28}N_3OP$ requires C, 77.17, H, 5.49, N, 8.18%).

Finally diazaphosphole *trans*-**1b** afforded phosphorane *trans*-**2b** (92%) (Rf 0.15) m.p. 175–177°C; i.r. ν_{max} 3441 (NH) cm^{-1},

^{31}P + 36.7 ppm; ^1H n.m.r δ3.31–4.02 (AB portion of an ABX system, 2H, CH_2), 4.10 (d, 1H, J(P—H), 10 Hz, CH), 4.72 (d, 1H, J(P—H) 21 Hz); MS 513 (M^+), 138 (100%). (Found: C, 77.25, H, 5.54, N, 8.14%).

When the above reactions were carried out in C_6D_6 the course of the reactions was periodically followed by ^1H n.m.r. spectroscopy. The doublet due to the methine proton of the starting phosphine **1** was slowly replaced by two doublets corresponding to the methine and NH protons of spirophosphorane **2**. No evidence of any signals due to the intermediate phosphazene **4** could be obtained.

Isomerization of Phosphoranes **2** *Under Acidic Conditions*

Cis- and *trans*-**2b** were found to be configurationally stable in benzene solutions at room temperature for several days. However when $CDCl_3$ solutions of pure *cis*- or *trans*-**2b** were allowed to stand at room temperature for 1–2 days a slow isomerization to *trans* or *cis*-**2b** respectively was detectable (t.l.c. and ^1H n.m.r.) Analogous trend was observed in CD_2Cl_2 solutions. When trace amounts of hydrogen chloride were bubbled in benzene solutions of *cis* and *trans*-**2b** some isomerization could be detected also in such cases. Similar trend was observed for *cis*- and *trans*-**2a** in benzene solutions containing small amounts of hydrogen chloride.

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8. The term "ligand" is reserved for the atom directly bonded to the phosphorus. See: F. Ramirez and J. Ugi, *Bull. Soc. Chim. Fr.*, 453 (1974) and references cited therein.
9. Although *cis*-**1** is used here to outline the proposed mechanism analogous Scheme would apply to the *trans*-**1**-isomer.