The reaction of λ^3-cyclotriphosphazanes with tetrachloro-*ortho*-benzoquinone: an unusual ring contraction–rearrangement

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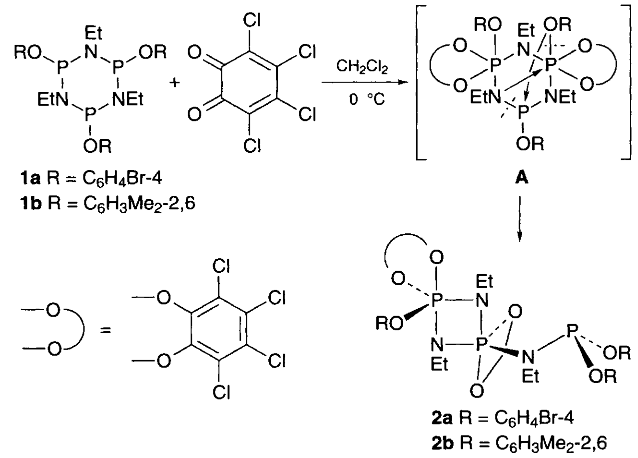
Oxidative addition of tetrachloro-*ortho*-benzoquinone to λ^3-cyclotriphosphazanes, [EtNP(OR)]$_3$ results in an unprecedented ring contraction–rearrangement to give diazadiphosphetidines $(EtN)_2[P(OR)(O_2C_6Cl_4)][P(O_2C_6Cl_4)\{N(Et)P(OR)_2\}]$ (R = C_6H_4Br-4 or $C_6H_3Me_2$-2,6), a process indicated to be thermodynamically favourable on the basis of PM3 calculations.

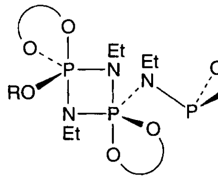
We had earlier proposed[1] that the product obtained from the reaction of the λ^3-cyclotriphosphazane [EtNP(OR)]$_3$ (**1a**; R = C_6H_4Br-4) with tetrachloro-*ortho*-benzoquinone (TOB) was a cyclotriphosphazane with two pentacoordinated phosphorus centres (**A**; R = C_6H_4Br-4) on the basis of elemental analysis and ^{31}P NMR data. We now report that the product is in fact a diazadiphosphetidine **2a** resulting from a ring contraction and rearrangement. This intriguing transformation is depicted in Scheme 1 and probably occurs *via* an intermediate of type **A**.



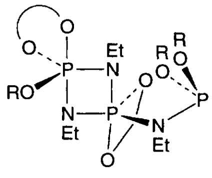
Scheme 1

The structure of related compound **2b** was confirmed by single crystal X-ray analysis.† Compounds **2a** and **b** are colourless, high-melting point solids (mp > 210 °C) stable to air and moisture.‡ Their ^{31}P NMR spectra show the presence of two isomers in each case. There are two sets of AMX patterns with J_{AX} = 0 Hz; the chemical shifts of A and M nuclei lie in a region characteristic of pentacoordinated phosphorus whereas the X chemical shift is in the tricoordinated region. The presence of two isomers is also evident from the ^1H NMR spectra; two distinct sets of signals (intensity ratio 2 : 1) arising from the ethyl group attached to the acyclic nitrogen atoms (and the methyl groups attached to the aryloxy substituents of **2b**) are observed. Tricyclic dispirodiazadiphosphetidines generally exist as *gauche* and *trans* isomers in solution.[2] Hence, the major isomer in solution may be assigned the *gauche* configuration as found in the solid state. The other isomer could have either the *trans* configuration **B** or *gauche* configuration **C** in which the two aryloxides of the λ^3-phosphorus point towards the four-membered ring.

The solid-state structure of **2b** consists of a planar four-membered P_2N_2 ring with the substituents at P(1) and P(2) *cis* to each other (*gauche*) (see Fig. 1). The four-membered ring consists of alternate long [P(1)–N(2) = 1.725(3), P(2)–N(1) = 1.745(3) Å] and short [P(1)–N(1) = 1.635(3), P(2)–N(2) = 1.639(2) Å] P–N bonds. The geometry around the two ring



B



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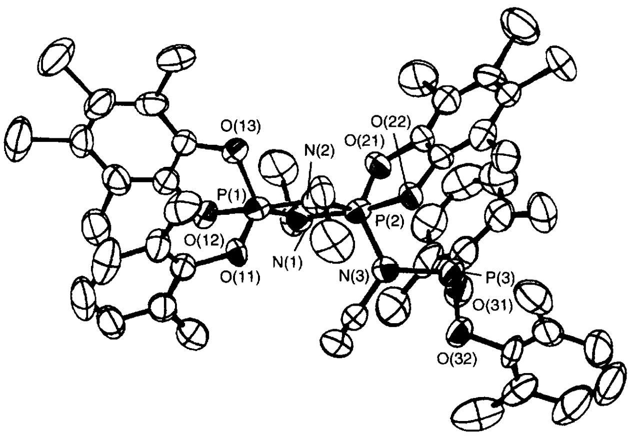

Fig. 1 Molecular structure of **2b**. Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.635(3), P(1)–N(2) 1.725(3), P(2)–N(2) 1.639(2), P(2)–N(1) 1.745(3), P(2)–N(3) 1.683(2), P(3)–N(3) 1.708(2); N(1)–P(1)–N(2) 80.62(12), N(2)–P(2)–N(1) 79.89(12), P(1)–N(1)–P(2) 99.41(13), P(2)–N(2)–P(1) 100.07(13), P(2)–N(3)–P(3) 119.02(14), N(2)–P(1)–O(12) 171.84(11), O(22)–P(2)–N(1) 169.45(10).

Table 1 Results of PM3 calculations on $(NH)_3P(OH)[P(OH)(O_2C_2H_2)]_2$ as models for **A** and **2**

Ring size	Ring conformation	Orientation of endocyclic NH	Isomeric configuration	Relative energy/ kcal mol^{-1}
6	boat	(a–e)[a]	*trans*	12.8
6	boat	(a–e)	*cis*	14.6
6	chair	(a–e)	*cis*	14.9
6	chair	(a–e)	*trans*	18.7
6	pseudo boat	(e–e)	*trans*	17.6
4	planar	(a–e)	*gauche*	0.0[b]
4	planar	(a–e)	*trans*	0.0[b]

[a] a = apical; e = equatorial. [b] Heat of formation = −321.7 kcal mol^{-1}. 1 cal = 4.184J.

phosphorus atoms is close to a trigonal bipyramid; at P(1), O(12) and N(2) occupy the apical positions while around P(2), O(22) and N(1) occupy the apical positions. The ring and acyclic nitrogen atoms display nearly planar geometries. The acyclic phosphorus atom, P(3) is highly pyramidal ($\Sigma° = 294.9°$) and its bond distance to N(3), [1.708(2) Å] is longer than the P–N bonds connected to the F_2P or O_2P unit in diphosphinoamines of the type $X_2PN(R)PY_2$.[3]

In order to gain an insight into the ring–ring transformation, PM3 calculations[4] have been carried out on different configurational and conformational isomers of $(NH)_3P(OH)[P(OH)(O_2C_2H_2)]_2$ as a model system for **A** and **2**. The ring contraction is computed to be thermodynamically favourable by 13–19 kcal mol^{-1} (see Table 1). Evidently, an apical and equatorial bond of a pentacoordinated phosphorus can be readily accommodated in a four-membered ring without severe strain. A further driving force for the rearrangement is a possible 'transannular interaction' of the oxygen of OH group with the λ^3-phosphorus as revealed by the optimised geometries; this non-bonded distance in the various possible six-membered ring conformers of **A** is 3.1–4.0 Å.

Zeiss and co-workers[5] have noted that the λ^3-cyclotriphosphazane $[MeNP(NEt_2)]_3$, when heated under vacuum at 100–105 °C gives the λ^3-cyclodiphosphazane $[MeNP(NEt_2)]_2$ as inferred from ^{31}P NMR spectroscopic data. Oxidative addition of chlorine to $[EtNPCl]_3$ gives the λ^5-cyclodiphosphazane $[EtNPCl_3]_2$.[6] Depending on the substituents on the phosphorus atoms, oxidative addition of TOB to 1,5,2,4-diazadiphosphorinan-6-ones bearing tricoordinated phosphorus centres leads to either retention of the six membered ring with tetra- and hexa-coordinated phosphorus centres or cleavage of the ring to give rearranged products in which the phosphorus has a coordination number four to six.[7] Recently, Quin and co-workers[8] have found that oxidative addition of TOB to the λ^3-trioxophosphorinane $[(RO)PO]_3$ ($R = C_6H_2Bu^t{}_2$-2,6-Me-4) results in the cleavage of the six-membered ring to give $[(RO)P(O)(O_2C_6Cl_4)]$. Our results constitute a new type of ring contraction–rearrangement reaction in cyclotriphosphazane chemistry.

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Footnotes

† *Crystal data* for **2b**: $C_{42}H_{42}Cl_8N_3O_7P_3$, triclinic, space group $P\bar{1}$, a = 11.858(1), b = 15.278(3), c = 15.230(3) Å, α = 101.37(2), β = 105.92(1), γ = 110.96(1)°, V = 2340.0(7) Å^3, Z = 2, D_c = 1.529 g cm^{-3}, μ(Mo-Kα) = 0.637 mm^{-1}, λ = 0.71073 Å, data collected at 163(2) K, Siemens P4 diffractometer. The structure was solved by direct methods using SHELXS-86 (G. M. Sheldrick, Universität Göttingen, 1990) and refined by full-matrix methods against the $F_o{}^2$ data employing SHELXL-93 (G. M. Sheldrick, Universität Göttingen, 1993) program; the hydrogen atoms were allowed to ride on the attached atoms during refinements, ω scan, $2\theta_{max}$ = 50°; total number of reflections = 6553, number of independent reflections = 5677, T_{min} = 0.5581, T_{max} = 0.5998, number of parameters = 577, GOOF = 0.971, final $wR2$ = 0.084, and R = 0.034 for 4566 reflections with $I > 2\sigma(I)$, the maximum/minimum residual electron density: 0.284/−0.413 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/86.

‡ Correct C, H, and N analyses were obtained for **2a** and **2b**.

Synthesis of **2**: A solution of **1**[9] (1.25 mmol) in CH_2Cl_2 (10 ml) was slowly added in drops to TOB (2.5 mmol) in CH_2Cl_2 (20 ml) at 0 °C under nitrogen atmosphere. The reaction mixture was warmed to 25 °C and stirred for 24 h. Solvent was removed under reduced pressure; the residue was washed with cold light petroleum (bp 60–80 °C) to remove any unreacted starting material **1**. The petroleum-insoluble material was crystallised from toluene (**2b**) or *o*-dichlorobenzene (**2a**) at 25 °C to obtain colourless crystals of **2** (**2a** yield 60%; **2b** yield 55%). When the reaction was carried out using 1 : 1 stoichiometry of **1** and TOB, **2** was isolated in 30% yield along with unreacted **1**. *Spectral data* for **2b**: ^{31}P NMR (161.3 MHz; $CDCl_3$, 25 °C; H_3PO_4) Isomer I (*gauche*): δ −52.84 (P^V, d, A), −46.26 (P^V, dd, M), 142.79 (P^{III}, d, X) [^2J(A, X) 0, ^2J(A, M) 166.8, ^2J(M, X) 81.5 Hz]; Isomer II: δ −54.87 (P^V, d, A′), −45.18 (P^V, dd, M′), 140.33 (P^{III}, d, X′) [^2J(A′, X′) 0. ^2J(A′, M′) 164.1, ^2J(M′, X′) 99.0 Hz]. ^1H NMR (400 MHz; $CDCl_3$, 25 °C, TMS) Isomer I (*gauche*): δ 1.19 (6 H, t, J 6.9 Hz, ring NCH_2CH_3), 1.65 (3 H, t, J 6.9 Hz, acyclic NCH_2CH_3), 2.17 and 2.30 (18 H, s, *o*-CH_3), 3.23–3.39 (4 H,br, ring NCH_2CH_3), 3.90–3.97 (2 H, br, acyclic NCH_2CH_3); Isomer II: δ 1.17 (6 H, t, J 7.2 Hz, ring NCH_2CH_3), 1.39 (3 H, t, J 7.1 Hz, acyclic NCH_2CH_3), 2.06 and 2.10 (18 H, s, *o*-CH_3), 3.07–3.21 (4 H, br, ring NCH_2CH_3), 3.58–3.65 (2 H, br, acyclic NCH_2CH_3); δ 6.84–7.25 (18 H, m, $OC_6H_3Me_2$-2,6, Isomers I and II). The ^{31}P and ^1H NMR spectra of **2a** displayed similar features to those observed for **2b**.

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