

Formation of phosphonates and pyrophosphates in the reactions of chlorophosphate esters with strong organic bases

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Abstract. The compounds $S(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O})_2\text{P(O)Cl}$ (**1**), $\text{CH}_2(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O})_2\text{P(O)Cl}$ (**2**) and $(2,2'\text{-C}_{20}\text{H}_{12}\text{O}_2)\text{P(O)Cl}$ (**3**) react with diazabicycloundecene (DBU) to give rise to, predominantly, the phosphonate compounds $[\text{S}(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O})_2\text{P(O)(DBU)}]^+\text{[Cl]}^-$ (**4**), $[\text{CH}_2(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O})_2\text{P(O)(DBU)}]^+\text{[Cl]}^-$ (**5**) and $[(2,2'\text{-C}_{20}\text{H}_{12}\text{O}_2)\text{P(O)(DBU)}]^+\text{[Cl]}^-$ (**6**). The first two compounds could be isolated in the pure state. In analogous reactions of **1** and **2** with diazabicyclononene (DBN) or N-methyl imidazole, only the pyrophosphates $[\text{S}(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O})_2\text{P(O)}]_2\text{O}$ (**7**) and $[\text{CH}_2(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O})_2\text{P(O)}]_2\text{O}$ (**8**) could be isolated, although the reaction mixture showed several other compounds in the phosphorus NMR. A possible pathway for the formation of phosphonate salts is proposed. The X-ray crystal structures of **4**, **7** and **8** are also discussed.

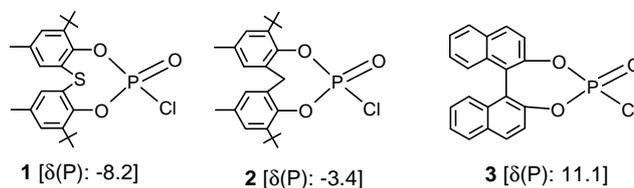
Keywords. Phosphonate salts; pyrophosphate esters; X-ray crystal structure.

1. Introduction

Nucleophilic substitution reactions of chlorophosphates are most often carried out in the presence of a base. In the absence of the base, this reaction will be slow and sometimes the base itself acts as a nucleophilic catalyst. The mechanism of rate enhancement (nucleophilic catalysis) of the nucleophilic substitution at phosphorus is commonly interpreted by two consecutive $S_N2(P)$ reactions (scheme 1).^{1–3} The leaving group X is substituted by the nucleophilic catalyst (Cat; can be N-methyl imidazole, imidazole or other bases) leading to a very reactive intermediate (**I**). The nucleophile then reacts with this intermediate giving the product. Although a species of type **I** has never been detected when the mixture of alcohol and catalyst was added to chlorophosphates, it is identified by NMR in the absence of alcohol. In the reaction of $(\text{RO})(\text{RCH}_2\text{O})\text{P(O)Cl}$ with the catalyst (Cat), formation of betaine **III** is observed and is assumed to occur *via* the intermediate **II**⁴. In the reaction of $(\text{EtO})_2\text{P(O)Cl}$ with N-methyl imidazole, Corriu and coworkers have identified three products (**IV–VI**); salts **IV–V** (not isolated) are similar to **II** and **III**². We have been interested in identifying/isolat-

ing intermediates of types **I–III**. One of the bases used by earlier workers was 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), but in a preliminary study we showed that this base could lead to phosphonate salts instead of betaines of type **I**⁵. Since such a product was never reported prior to our work, we were curious to know whether this feature is common for other chlorophosphate esters also and hence we have extended this study. The results are reported here.

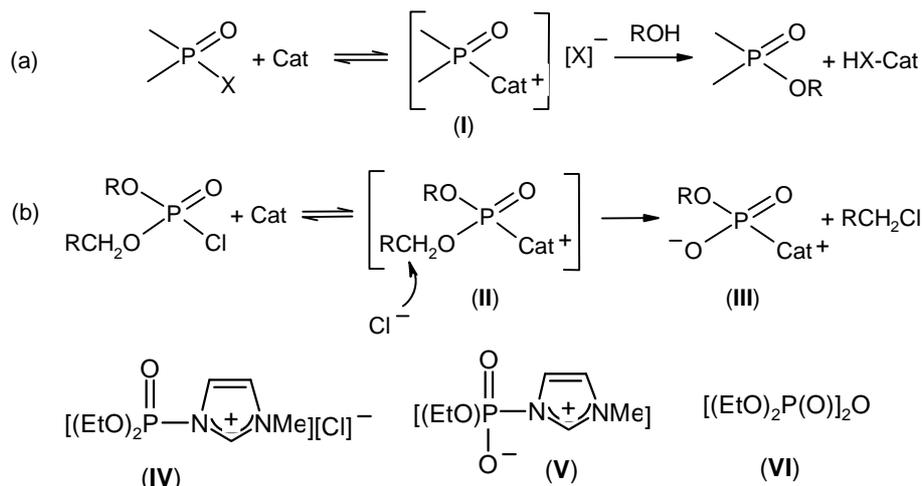
We have chosen, primarily, DBU, DBN [1,5-diazabicyclo(4.3.0)non-5-ene] and N-methyl imidazole, all with two nitrogen atoms as bases and compounds **1–3**^{5–8} as phosphorus substrates.



2. Experimental section

Chemicals were procured from Aldrich/Fluka or local manufacturers; they were purified when required. Solvents were purified according to standard proce-

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Scheme 1.

dures.⁹ All reactions, unless stated otherwise, were performed under dry nitrogen atmosphere. ¹H and ³¹P{H} NMR spectra were recorded on a Bruker 200 or 400 MHz spectrometer in CDCl₃, with shifts referenced to SiMe₄ (*d* = 0) or 85% H₃PO₄ (*d* = 0). Elemental analyses were carried out on a Thermo Finnigan EA1112 analyser.

2.1 Synthesis of [S(6-*t*-Bu-4-Me-C₆H₂O)₂P(O)](DBU)]⁺[Cl]⁻ (**4**)

To a stirred solution of S(6-*t*-Bu-4-Me-C₆H₂O)₂P(O)Cl⁶ (**1**) (0.84 g, 1.90 mmol) in toluene (20 ml) was added DBU (0.29 g, 1.90 mmol) dropwise over a period of 10 min at room temperature. After stirring overnight, most of the solvent was removed in *vacuo* and the compound crystallized from dichloromethane–heptane (2 : 1) mixture. Yield (isolated): 0.5 g (45%). m.p.: 210°C. IR (KBr): 3410, 3198, 2955, 1641, 1427, 1265, 1224 cm⁻¹. ¹H NMR: *d* 1.35, 1.46 (2s, 18H, Ar-C(CH₃)₃), 1.90–2.00 (*m*, 8H, CH₂), 2.27, 2.31 (2s, 6H, ArCH₃), 3.40–3.60 (*m*, 6H, NCH₂), 7.12–7.48 (*m*, 4H, Ar-H), 11.3 (*br*, 1H, NH). ¹³C NMR: *d* 19.2, 19.5, 20.7, 20.7, 20.9, 21.4, 24.0, 24.5, 25.1, 26.4, 26.8, 29.5, 29.9, 35.0, 35.1, 38.5, 44.3 [¹J(P-C) = 130.9 Hz], 50.4, 53.5, 53.8, 124.4, 125.1, 125.2, 128.1, 128.9, 129.6, 130.2, 134.7, 135.1, 135.3, 148.7, 148.9, 149.5, 149.6, 160.6. ³¹P NMR: *d* 6.4. The reaction mixture also showed peaks at *d* -12.8 (10%) and -22.0 (5%) in the ³¹P NMR. Analysis: Calcd. for C₃₀H₄₄ClN₂O₃PS (after drying): C, 62.22; H, 7.61; N, 4.84%; Found: C, 61.95; H, 7.38; N, 4.62%.

The compound [CH₂(6-*t*-Bu-4-Me-C₆H₂O)₂P(O)](DBU)]⁺[Cl]⁻ (**5**) [m.p. 220°C] was prepared similarly; its ¹H and ³¹P NMR [*d* 7.2] were identical to

the one we have reported earlier⁵. We have tried to check its identity by ¹³C NMR also but a detailed analysis was not possible: *d* 19.2, 19.6, 20.8, 21.3, 24.0, 24.4, 25.3, 26.8, 28.9, 31.0, 31.3, 32.1, 34.6, 34.8, 34.9, 39.1 [¹J(PC) = 126.0 Hz, by comparing the spectrum with that for **4**], 43.1, 48.8, 49.3, 52.6, 54.4, 125.3, 127.3, 127.4, 128.2, 129.0, 129.2, 134.1, 134.4, 135.3, 137.8, 140.2, 144.7, 161.0. Analysis: Calcd. for C₃₁H₄₆ClN₂O₃P: C, 66.38, H, 8.21, N, 5.00%. Found: C, 66.56, H, 7.99, N, 4.31.

The reaction of (2,2'-C₂₀H₁₂O₂)P(O)Cl (**3**, racemic)⁸ with DBU was conducted in THF, because of low solubility of **3** in toluene. The ³¹P NMR spectrum showed three peaks at *d* 5.3 (25%), 29.2 (30%) and 30.4 (40%) [rest ~ 5%]. The peaks at *d* 29.2 and 30.4 are assigned to the diastomeric phosphonate salts [(2,2'-C₂₀H₁₂O₂)P(O)(DBU)]⁺[Cl]⁻ (**6**) by comparing them with those for the analogous aminophosphonate (+)-(C₂₀H₁₂O₂)P(O)CHNHCO₂EtPh [*d*(P) 29.5]¹⁰. A white solid with *d*(P) 5.3 (>95%), that showed only the binol and DBU residues, was isolated in the reaction of **3** with DBU in the presence of (OCH₂CMe₂CH₂O)P(O)CH(OH)(C₆H₄-OCMe). This solid could not be purified further, but is likely to be the phosphate salt (2,2'-C₂₀H₁₂O₂)P(O)(O⁻)[HDBU⁺] formed by hydrolysis [¹H NMR shows a peak at *d* 10.9; ¹³C NMR: complicated, but no doublet due to ¹J(PC) is observed].

2.2 Reaction of S(6-*t*-Bu-4-Me-C₆H₂O)₂P(O)Cl (**1**) with DBN – Preparation of the pyrophosphate ester

[S(6-*t*-Bu-4-Me-C₆H₂O)₂P(O)]₂O (**7**): To a stirred solution of **1**¹ (0.85 g, 1.94 mmol) in toluene (20 ml) was added DBN (0.24 g, 1.94 mmol) drop-wise over a

period of 10 min at room temperature. After stirring overnight the solvent was removed *in vacuo* and the compound crystallized from dichloromethane–heptane (2 : 1) mixture. In this reaction we obtained the crystals of the pyrophosphate [S{6-*t*-Bu-4-Me-C₆H₂O}P(O)]₂O (**7**) but not of the expected compound. m.p.: 226–228°C. IR (KBr): 2961, 2359, 1593, 1429, 1319, 1222 cm⁻¹. ¹H NMR: **d** 1.39, 1.46 (*s* each, 36 H, Ar-C(CH₃)₃), 2.29 (2*s*, 12H, ArCH₃), 7.20, 7.25 (2*s*, 8H, Ar-H). ¹³C NMR: **d** 20.8 (*s*, ArCH₃), 30.3 (Ar-C(CH₃)₃), 35.1 (Ar-C(CH₃)₃), 124.7, 129.9, 134.2, 135.0, 141.6, 150.0. ³¹P NMR: **d** –31.1. Analysis: Calcd. for C₄₄H₅₆O₅P₂S₂ (after drying): C, 66.84; H, 7.09. Found: C, 66.95, H, 6.98%.

Reaction using N-methyl imidazole also resulted in the isolation of **7**.

The reactions of **2** and **3** with DBN and N-methyl imidazole were done similarly, but in the latter case, THF was used as the solvent. ³¹P NMR (major peaks, **d**): (a) **2** + DBN: –9.8 (46%), 0.1 (47%); (b) **2** + N-methyl imidazole: –2.3 (65%), –9.8 (15%), –27.6 (20%); (c) **3** + DBN: –12.4 (30%), 3.2 (30%) and 14.8 (30%); (d) **3** + N-methyl imidazole: –12.4 (70%), 6.1 (28%). The peak at **d** –27.6 in (b) is due to the pyrophosphate ester [CH₂(6-*t*-Bu-4-Me-C₆H₂O)₂P(O)]₂O (**8**) and could be isolated in ≈ 40% yield [m.p. 276°C; ¹H NMR: Identical to that reported earlier⁵; ¹³C NMR **d** 20.9, 30.9, 34.6, 35.0, 127.7, 129.4, 131.4, 135.2, 141.3, 146.0. Analysis: Calcd. for C₄₆H₆₀O₇P: C, 70.23; H, 7.63. Found: C, 70.43, H, 7.81]. The peak at –12.4 in (c) and (d) is also assignable to the pyrophosphate ester [(2,2'-C₂₀H₁₆O₂)P(O)]₂O on the same basis, but this compound was hydrolytically unstable [NMR evidence].

2.3 X-ray structural analysis of **4**, **7** and **8**

X-ray data were collected on a Bruker AXS SMART diffractometer (for **4** and **7**) or an Enraf-Nonius-MACH3 (for **8**; upto 2 θ = 45) using Mo-K α (I = 0.71073 Å) radiation. The structures were solved by direct methods¹¹; all non-hydrogen atoms were refined anisotropically. For the hydrogen atoms except the NH in **4**, the riding model was used; one of the solvent hydrogen atoms in **4** was not fixed because of symmetry. In **8** although there is a void and some residual electron density in the crystal packing, we could not model it with any suitable solvent; for this compound, we had given only the crystal data before⁵, but the refinement could be improved and hence structure is better now. Data were not good because of the poor crystal quality.

Crystal data: Compound **4**. CH₂Cl₂.1/2C₆H₅CH₃: C₇₁H₁₀₀Cl₆N₄O₆P₂S₂, M = 1444.30, triclinic, space group $P\bar{1}$, a = 9.521(1), b = 14.310(1), c = 14.533(1), α = 93.432(1), β = 92.521(1), γ = 98.959(1), V = 1949.6(2) Å³, Z = 1, ρ = 1.230 g cm⁻³, F_{000} = 766, m = 0.364 mm⁻¹, Data/restraints/parameters: 9130/5/427. S (all data) = 0.981. R indices ($I > 2s(I)$): RI = 0.0535, $wR2$ (all data) = 0.1714. Max./min. residual electron density ($e\text{\AA}^{-3}$) 0.547/–0.403. Compound **7**. CH₂Cl₂: C₄₅H₅₈Cl₂O₇P₂S₂, M = 907.87, monoclinic, space group $P2/n$. a = 12.509(1), b = 9.449(1), c = 20.606(2), β = 91.003(1), V = 2435.2(3) Å³, Z = 2, ρ = 1.238 g cm⁻³, $F(000)$ = 960, m = 0.330 mm⁻¹, Data/restraints/parameters: 5852/3/276. S (all data) = 1.038, R indices ($I > 2s(I)$): RI = 0.0590, $wR2$ (all data) = 0.1922. Max./min. residual electron density ($e\text{\AA}^{-3}$) 0.510/–0.411. Compound **8**: C₄₆H₆₀O₇P₂, M = 786.88, tetragonal, space group $P-4$. a = b = 15.996(2), c = 9.323(1), V = 2385.4(5) Å³, Z = 2, ρ = 1.096 g cm⁻³, $F(000)$ = 844, m = 0.135 mm⁻¹, Flack parameter (employing the WINGX programme using the twin command¹²) = 0.0. Data/restraints/parameters: 3103/0/249. S (all data) = 1.140, R indices ($I > 2s(I)$): RI = 0.0577, $wR2$ (all data) = 0.1846. Max./min. residual electron density ($e\text{\AA}^{-3}$) 0.621/–0.225. Further details as CIF files are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers CCDC 245230–245232.

3. Results and discussion

The reaction of **1–3** with DBU is conducted in toluene (or THF for **3**) as the solvent. Phosphonate salts **4–6** are the major products. Compounds **4–5** could be isolated as pure solids. In the case of **6**, two isomeric products [**d**(P) 29.4, 30.0; probably diastereomeric] are formed along with another product that showed a **d**(P) of 5.4. As mentioned in our earlier communication, assignment of structure for compound **5** could be done mainly by its downfield ³¹P NMR chemical shift⁵; the ¹³C NMR is complex and in the ¹H NMR, a broad resonance appeared at **d** 11.48 (ascribable to NH proton). The spectral features of **4** were analogous to those for **5**, but in this case the P-CH carbon was more readily diagnosed at **d** 44.4 [¹ J (PC) = 130.0 Hz] in high-field ¹³C NMR. For further confirmation, we have studied compound **4** by X-ray structure determination (figure 1). Attempted dehydrohalogenation of **4** in methanolic NaOH gave a mixture that showed two major peaks (total

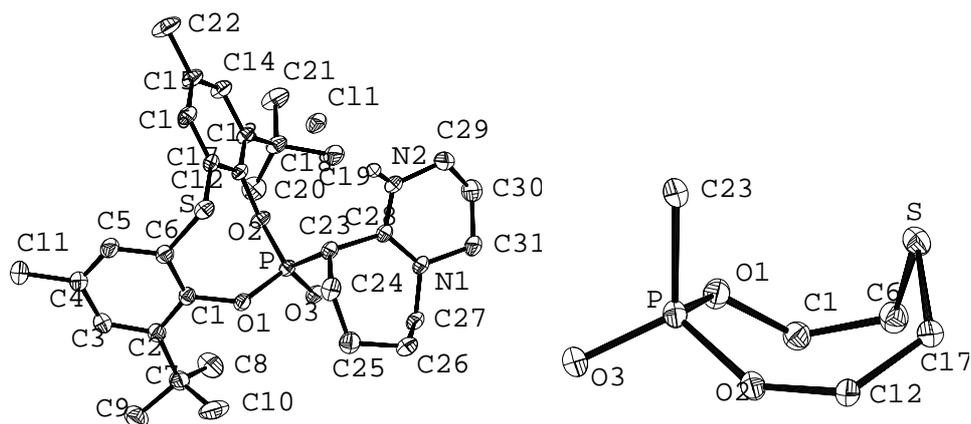
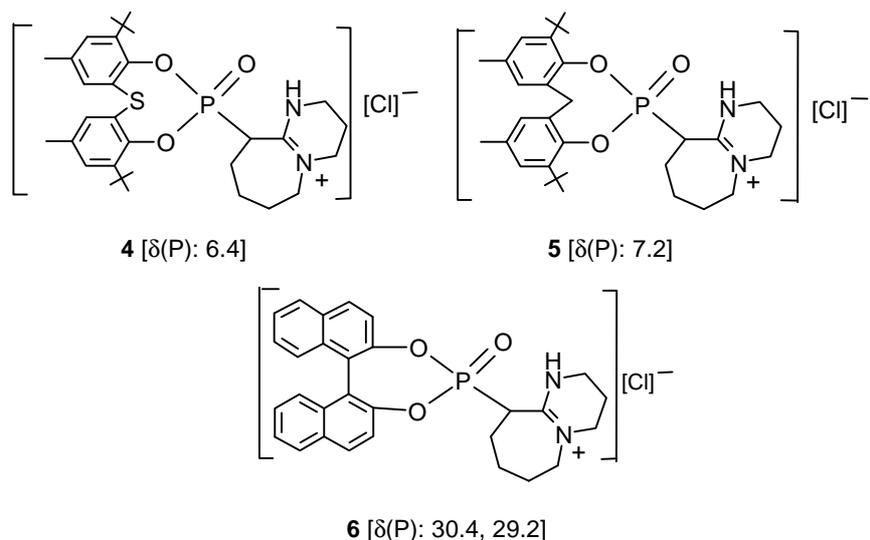


Figure 1. An ORTEP drawing of **4**. $\text{CH}_2\text{Cl}_2 \cdot 1/2\text{C}_6\text{H}_5\text{CH}_3$, solvent molecules are omitted. On the right hand side is shown the conformation of the eight-membered phosphocin ring. Selected bond distances (\AA): P–O(1) 1.583(2), P–O(2) 1.568(2), P–O(3) 1.460(2), P–C(23) 1.822(3), N(1)–C(28) 1.328(3), N(2)–C(28) 1.303(3). Hydrogen bond parameters for N(2)–HN(2)–Cl(1): 0.72(3), 2.39(3) and 3.109(3) \AA and 171(3) $^\circ$.

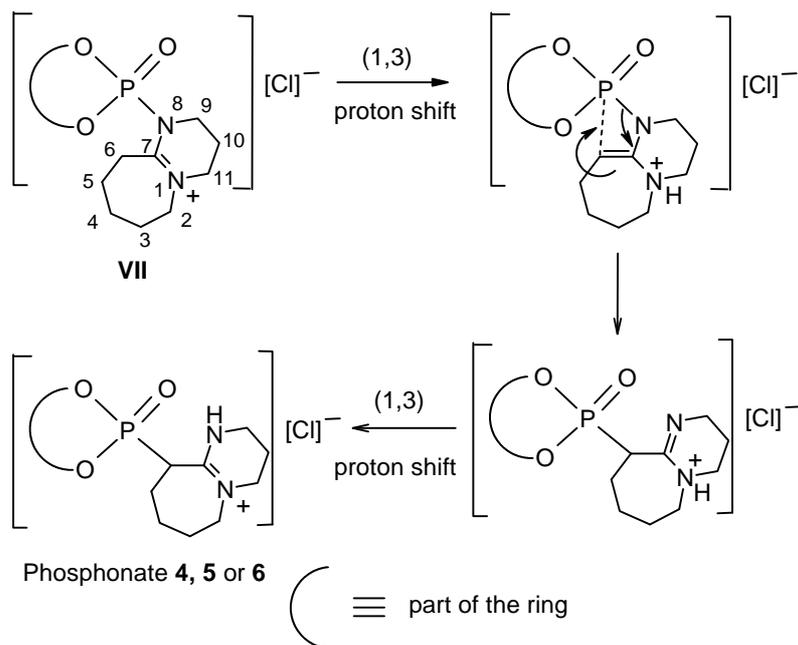


intensity > 85%) at **d** 24.8 and 31.4 (phosphonate region) in the ^{31}P NMR, but a pure compound could not be isolated.

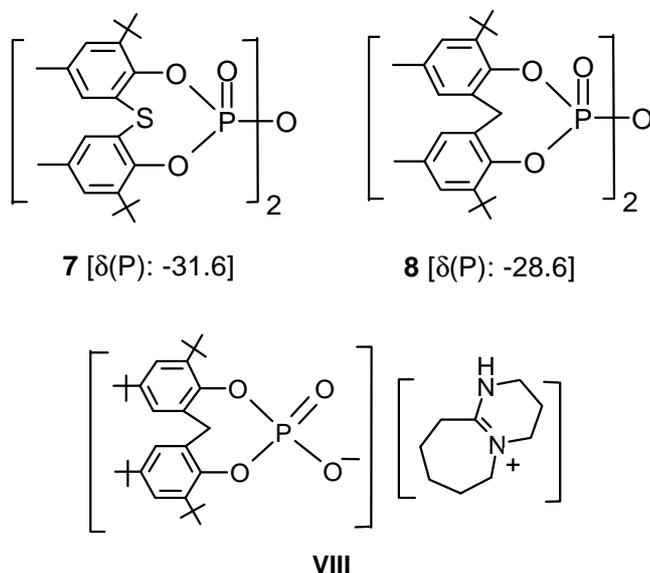
It is important to note that the use of DBU as a base is quite common and several studies using phosphate esters are also conducted in its presence¹³. To our knowledge, in these reports the possibility of formation of phosphonate salts is not mentioned, although it is known that DBU can be lithiated at the C(6) position (cf. scheme 2 for numbering)¹⁴. Formation of the phosphonate (cf. **4–6**), however, might have taken place *via* the intermediacy of a phosphoramidate salt **VII** that undergoes 1,3-proton shift from C-6 to N-1 to give an enamine. This enamine could re-

organize to **4** (or **5** or **6**) *via* a cyclic 4-membered transition state involving C-6, C-7, N-8 and P.

Although DBN is also a dinitrogen base similar to DBU, we did not observe a phosphonate salt in reactions using DBN. The reaction of **1** with DBN initially showed peaks at **d** –3.0, –11.4 and –12.1 in the ^{31}P NMR. However, the only product that could be isolated in a pure state was the pyrophosphate **7** [**d**(P) –31.1; this was not present in the original reaction mixture but formed over a period of time]. Even in the reaction using **2**, the analogous pyrophosphate **8** is a major product. In the reaction of **1** with N-methyl imidazole, the pyrophosphate (30%) along with two other peaks at **d** –7.0 and –11.7 are



Scheme 2.



observed in the ^{31}P NMR. The pyrophosphate is most likely produced by the reaction of the organophosphate salt (formed by the hydrolysis of phosphoramidate salt of type **VII**) with the chlorophosphate **1** or **2**. The ^{31}P NMR peak at -11.5 ± 0.2 ppm in the reaction of **1** with DBN or N-methyl imidazole is ascribable to the organophosphate salt $\text{S}(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O}_2)_2\text{P}(\text{O})(\text{O}^-)(\text{HBase}^+)$; for comparison, the

$d(\text{P})$ value for the analogous salt $\text{CH}_2(4,6-(t\text{-Bu})_2\text{C}_6\text{H}_2\text{O}_2)_2\text{P}(\text{O})(\text{O}^-)(\text{HDBU}^+)$ (**VIII**) is -11.4^{15} .

The ^{31}P NMR peak at $d-3.0$ or -7.0 in the reaction of **1** with DBN or N-methyl imidazole respectively, is likely to be due to the expected phosphoramidate salt. This assessment is based on our previous observation that in compounds containing the same eight-membered ring and phosphoryl oxygen, P-N bonded compounds show $d(\text{P})$ values in between those for P-O and P-C bonded ones. The peak with $d(\text{P}) -12.1$ (see above) is not assigned.

In the analogous reaction of **3** with DBN, several species are formed and the spectrum changed with time. A peak at $d-12.4$, ascribable to the pyrophosphate, was a major component after 3 days; even with N-methyl imidazole, this compound was the major product [^{31}P NMR].

3.1 Brief discussion of the structures

In the structure of **4** (figure 1), the phosphorus is connected to the carbon of the seven-membered ring that is at *b*-position to the nitrogen of the six-membered ring of the DBU residue. The P-O bond distances and the angles at phosphorus are in the normal range observed in similar compounds¹⁶. There is moderately strong hydrogen bonding between the

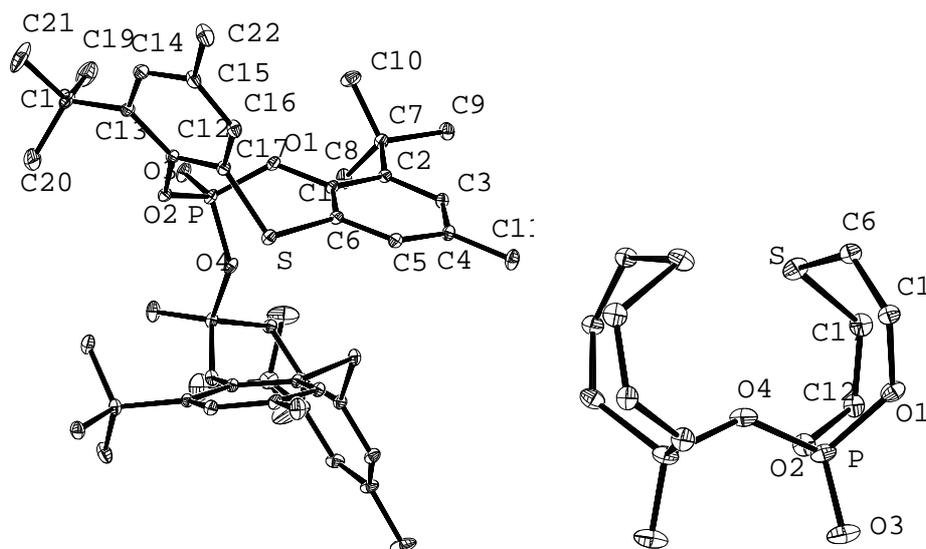


Figure 2. Molecular structure of **7**. CH_2Cl_2 solvent is not shown. Also shown on the right hand side is the conformation of the eight-membered ring. Selected distances and angles (\AA , $^\circ$): P–O(3) 1.443(2), P–O(1) 1.563(2), P–O(2) 1.567(2), P–O(4) 1.583(1), O(3)–P–O(1) 113.49(11), O(3)–P–O(2) 113.33(10), O(1)–P–O(2) 106.81(9), O(3)–P–O(4) 114.68(12), O(1)–P–O(4) 104.06(8), O(2)–P–O(4) 103.47(7), P–O(4)–P' 134.17(14).

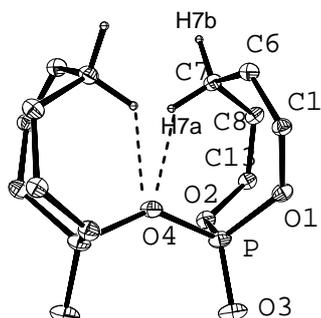


Figure 3. A picture showing the conformation of the phosphocin ring and possible interaction of the ArCH_2 hydrogen with the exocyclic non-phosphoryl oxygen in **8**. Other features are similar to that in **7** (*cf.* figure 3). Selected distances and angles (\AA , $^\circ$): P–O(1) 1.562(4), P–O(2) 1.563(4), P–O(3) 1.438(4), P–O(4) 1.591(2), O(3)–P–O(1) 113.1(3), O(3)–P–O(2) 114.4(2), O(1)–P–O(2) 106.6(2), O(3)–P–O(4) 115.1(3), O(1)–P–O(4) 103.60(19), O(2)–P–O(4) 102.83(17), P–O(4)–P' 135.4(4). C(7)–H(7a)...O(4) parameters: 0.97, 2.51, 3.197(7) \AA , 127.5 $^\circ$.

N(2)–H and the chloride ion (*cf.* figure 1). However, the short N(1)–C(28) bond distance shows that the double bond is delocalized. The intra-molecular non-bonded P...S distance is 3.33 \AA which is less than the sum of van der Waals radii, but longer than that in several hexacoordinate phosphoranes with the same ring residue^{6,17}. The eight-membered ring

has a *tub* conformation that is analogous to that observed in many other tetracoordinate phosphorus compounds containing the $\text{CH}_2(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O})_2$ P(O) group, but different from the *boat-chair* conformation observed for P(III) compounds with similar rings. In compound **7** (*cf.* figure 2), the intra-molecular P...S distance is 3.40 \AA and the conformation of the eight-membered ring is again *tub*. Earlier, we had suggested that observation of *tub* conformation in compounds with the $\text{CH}_2(6-t\text{-Bu-4-Me-C}_6\text{H}_2\text{O})_2$ P(O) group is related to the presence of weak intra-molecular C–H...O interactions between the ArCH_2 protons and the phosphoryl oxygen^{16,18} but such a feature is absent in **4** or **7** [In the absence of any additional interaction, the expected conformation is that of a *boat-chair*]¹⁹. The possible intra-molecular C–H...O contacts in compound **8** are shown in figure 3; here the bridging oxygen is closer to one of the ArCH_2 hydrogens and the conformation of the eight-membered ring is *tub*. A few more examples are necessary to conclude whether P...S (very weak, if at all) interaction in **4** or **7** has played a role (or not) in the observed *tub* conformation.

An interesting feature in **7** is the sulphur–sulphur non-bonded distance of ≈ 4.2 \AA within the molecule which suggests that **7** can be used as a soft bidentate ligand towards transition metals.

4. Summary

In this paper we have reported, primarily, the synthesis and structures of (i) the phosphonate **4** and (ii) the pyrophosphate **7**. The former result, in conjunction with our earlier observations, shows that in the reaction of chlorophosphates with DBU, formation of P–C bonded (phosphonate) compound is a major pathway. In the reaction with other bases, one of the major products is always the pyrophosphate ester, formed most likely *via* phosphoramidate salts. The larger 7-membered ring in DBU, compared to the 5-membered ring DBN, might have brought the **b** (to the nitrogen of the six-membered ring) carbon of this ring in close proximity to the phosphorus resulting in the isolation of phosphonate salts.

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