Bicyclic Phosphanes. Part 2.[1] Spontaneous Dimerization of a Constrained Bicyclic Phosphane. The Crystal and Molecular Structure of a Tricyclic Compound containing the Dioxadiazadiphosphecine Ring

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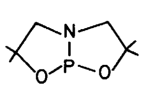
The dimerization of 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phospha$^{\rm III}$bicyclo[3.3.0]octane (1) leads to octahydro-2,2,6,6,10,10,14,14-octamethylbis-1,2,3-oxazaphospholo[2,3-*b*:2',3'-*g*]-1,6,3,8,2,7-dioxadiazadiphosphecine (2), a tricyclic compound with sixteen atoms around the periphery. The preparation, identification, and the *X*-ray structure are described. A pathway for the formation of the dimer is suggested by the *trans*-position of the two phosphorus lone pairs.

The polymerization of the organophosphorus compounds has long been studied and the polymers have been used for technical purposes.[2] One of the main problems in this field of research is the structure, linear or cyclic, of the oligomers derived from cyclic monomers. Remarkable progress was made when it was demonstrated that the 2-methyl-1,3,2-dioxaphosphorinan (3) is in equilibrium with its dimeric and trimeric forms, $(3)_{\rm dim}$ and $(3)_{\rm trim}$ with, respectively, 12- and 18-membered rings,[3] and when the corresponding thiono-derivatives were isolated. This investigation has been extended to many other examples. A recent paper on the dimerization of 2-phenyl-3-methyl-1,3,2-oxazaphospholane (4) cites the main references in this area.[4]

Among the rules and observations governing the oligomerization of cyclic phosphorus compounds we underline the following.

(i) The macrocyclisation process leads generally to equilibria between mono-, di-, tri-, and *n*-mers; (ii) distillation of polymerized samples usually allows quantitative recovery of monomer; (iii) ring expansion often depends upon minor experimental factors: moisture, impurities, nature of the storage vessel; (iv) step-by-step cyclisation is quite general and is observed for dioxaphosphocan, dioxaphosphepan, dioxaphosphorinan, and dioxaphospholan (respectively, eight-, seven-, six-, five-membered rings).

During our studies of constrained 2,8-dioxa-5-aza-1-phospha$^{\rm III}$bicyclo[3.3.0]octanes (5) we observed a tendency of these compounds towards oligomerization and established that this phenomenon depends upon the number and the nature of the substituents.[1] In this paper we describe an example of clear-cut dimerization leading to the isolation of compound (2), which is interesting for detailed studies and is original from several points of view: (i) the dimer is readily available, (ii) sulphurization of the tricovalent phosphorus atoms in order to isolate the dimer, as was the case with (3), is not necessary, and (iii) (2) appears as a pure diastereoisomer among six possible structures.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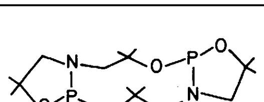
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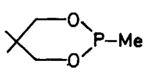
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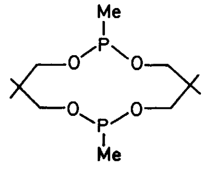
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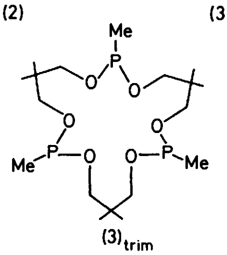
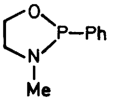

$(3)_{\rm trim}$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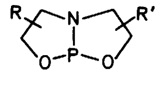
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Results and Discussion

Reaction of tris(dimethylamino)phosphane with 1,1,5,5-tetramethyl-3-azapentane-1,5-diol leads to two products as shown by the ^{31}P n.m.r. spectrum of the reaction mixture which exhibits two peaks at δ_1 163 and δ_2 140.8 p.p.m. Distillation at $<10^{-3}$ Torr allows two fractions to be separated, comprising (a) a non-viscous liquid whose ^{31}P n.m.r. spectrum contains only one peak at δ_1 163 p.p.m. and which was identified as the bicyclic phosphane (1) by mean of elemental analysis and n.m.r. spectroscopy (^{1}H and ^{13}C) and (b) a non-distillable solid whose ^{31}P n.m.r. spectrum (in benzene solution) contains only one peak at δ_2 140.8 p.p.m. It was identified as the dimer (2) by mean of mass spectroscopy, *m/e* 378 (M^+), and characterized by its ^{1}H n.m.r. spectrum. All the data are in agreement with the proposed structure (2). Recrystallisation in dry xylene gave suitable crystals for *X*-ray determination.

Crystallographic Data.—The parameters and the space group of compound (2) were determined using a Weisenberg camera. For data collection, the crystal, carefully selected, was mounted on an automatic Enraf-Nonius CAD 4 computer-controlled four-circle diffractometer. The crystallographic and physical data, as well as the measurement conditions, are given in Table 1.

The crystal and molecular structure of the dimer (2) were determined using the MULTAN 78 direct method.[5] Refinement of the position and thermal parameters of all non-hydrogen atoms was then performed. The hydrogen atoms were localized using Fourier synthesis. After attribution of isotropic thermal parameters $B_{1H} = 1.2B_{1C}$ to the hydrogen atoms, the R value dropped to $R = 0.033_7$.

The atomic co-ordinates of the non-hydrogen atoms are listed in Table 2 whereas the interatomic distances and bond angles are collected in Tables 3a and b. The distances of characteristic atoms from the principal mean planes are given

Table 1. Physical and crystallographic data of compound (2). Experimental conditions of crystallographic measurements

(1) Physical and crystallographic data

Formula, $(PO_2NC_8H_{16})_2$	Molecular weight, 378.389
Crystal system, monoclinic	Space group, $P2_1/n$
$a =$ 9.910(11) Å	$U =$ 1 019(1) Å^3
$b =$ 10.239(3) Å	$\beta =$ 97.24(6)°
$c =$ 10.129(12) Å	$Z = 2$
$\rho_{exp.} =$ 1.3(1) g cm^{-3}	$F(000) = 408$
	$\rho_X =$ 1.23 g cm^{-3}

(2) Data collection

Temperature, −50 °C

Radiation, molybdenum (K_α)

Maximum Bragg angle 30°

Values determining the scan speed

SIGPRE[a] 0.750, SIGMA[a] 0.018, VPRE[a] 10° min^{-1}, TMAX[a] 80 s

(3) Conditions for refinement

Reflections for the refinement of the cell dimensions, 25

Recorded reflections, 2 721

Independent reflections, 2 632

Utilized reflections, 2 556

Refined parameters, 109

Reliability factors,

$$R = \Sigma|k|F_o| < |F_c|/\Sigma|k|F_o| = 0.0337,$$
$$R_w = [\Sigma w(k|F_o| < |F_c|)^2/\Sigma wk^2F_o{}^2]^{1/2} = 0.0414$$

[a] The definition of these parameters is given in ref. 5.

Table 2. Atomic co-ordinates

Atom	x	y	z
P(16)	0.584 13(4)	0.156 97(4)	0.039 04(4)
O(1)	0.704 8(1)	0.262 7(1)	0.028 7(1)
O(15)	0.656 2(1)	0.017 7(1)	0.002 8(1)
N(4)	0.506 5(1)	0.196 5(1)	−0.114 9(1)
C(2)	0.716 5(2)	0.313 4(2)	−0.104 1(2)
C(3)	0.610 0(2)	0.238 4(2)	−0.197 1(2)
C(13)	0.599 7(2)	−0.116 5(2)	0.188 6(2)
C(14)	0.711 7(2)	−0.071 0(2)	0.108 9(2)
C(17)	0.860 2(2)	0.289 0(3)	−0.133 7(3)
C(18)	0.685 0(3)	0.458 4(2)	−0.099 9(2)
C(19)	0.772 9(2)	−0.183 4(2)	0.037 8(2)
C(20)	0.822 5(2)	−0.001 8(2)	0.201 8(2)

in Table 4. Structure factors and thermal and positional parameters are given in Supplementary Publication No. SUP 23534 (16 pp.).*

Structure.—The molecule is centrosymmetric and organized around a crystallographic symmetry centre. Figure 1 shows a perspective view, the hydrogen atoms being omitted for clarity. With Figure 1 and Tables 3a, 3b, and 4 we can make the following points.

The formation of only one dimer, suggested by n.m.r. data, is confirmed by the *X*-ray structural analysis. As the dimer results from the association of two monomers through a bond rupture–formation process and since this process can occur with two P–O bonds or two P–N bonds or one P–O and one P–N bond, the expected structural isomers belong to three different sets: (i) homodimers from P–O bonds, (ii) homodimers from P–N bonds, (iii) heterodimers (Scheme).

Table 3.

a Interatomic distances (Å)[a]

P(16)–O(1)	1.626 2(12)	P(16)–O(15)	1.656 6(13)
P(16)–N(4)	1.698 5(13)	O(1)–C(2)	1.459 8(21)
O(15)–C(14)	1.460 1(18)	N(4)–C(13)	1.462 2(19)
N(4)–C(3)	1.465 4(20)	C(2)–C(17)	1.512 8(28)
C(2)–C(18)	1.523 4(28)	C(2)–C(3)	1.529 7(23)
C(13)–C(14)	1.525 0(22)	C(14)–C(19)	1.523 9(24)
C(14)–C(20)	1.528 0(23)		

b Bond angles (°)

O(1)–P(16)–O(15)	102.57(6)	O(1)–P(16)–N(4)	91.94(6)
O(15)–P(16)–N(4)	99.19(6)	C(2)–O(1)–P(16)	116.16(9)
C(14)–O(15)–P(16)	120.36(9)	C(5)–N(4)–C(3)	112.6(1)
C(5)–N(4)–P(16)	123.3(1)	C(3)–N(4)–P(16)	108.8(1)
O(1)–C(2)–C(17)	108.1(1)	O(1)–C(2)–C(18)	106.1(1)
O(1)–C(2)–C(3)	105.1(1)	C(17)–C(2)–C(18)	112.4(2)
C(17)–C(2)–C(3)	112.9(2)	C(18)–C(2)–C(3)	111.7(1)
N(4)–C(3)–C(2)	106.0(1)	N(12)–C(13)–C(14)	115.2(1)
O(15)–C(14)–C(19)	104.9(1)	O(15)–C(14)–C(13)	110.4(1)
O(15)–C(14)–C(20)	109.8(2)	C(19)–C(14)–C(13)	112.3(1)
C(19)–C(14)–C(20)	110.0(1)	C(13)–C(14)–C(20)	109.3(1)

[a] All C–H distances lie between 0.92 and 0.99 Å.

Table 4. Distances (Å) to the principal mean planes

Mean plane P(16)–N(4)–O(1)–C(2):

$$-0.5493x + 0.7744y + 0.3138z + 1.7256 = 0$$

P(16)	−0.059	N(4)	0.083
O(1)	0.082	C(2)	−0.091
C(3)	−0.464	C(17)	−1.182
C(18)	1.257		

Mean plane P(16)–P′(16)–N(4)–N′(4):

$$-0.8579x + 0.3204y + 0.4016z + 4.2512 = 0$$

P(16)	0	N(4)	0
O(15)	−1.255	C(14)	−1.474
C(13)	−0.262	O(1)	−0.732
C(3)	−1.164		

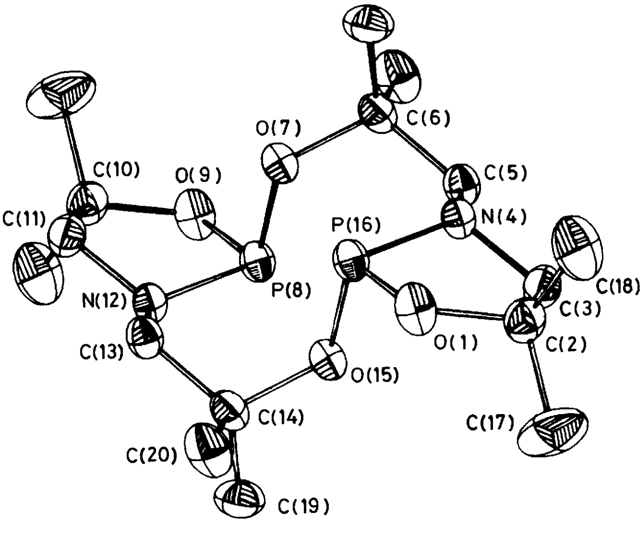

Figure 1. ORTEP representation of the tricyclic dimer (2)

In (i) the phosphorus lone pairs can be either *trans* (centrosymmetric structure) or *cis* (a chiral structure which has two enantiomers). For (ii) the caged model has only one (achiral)

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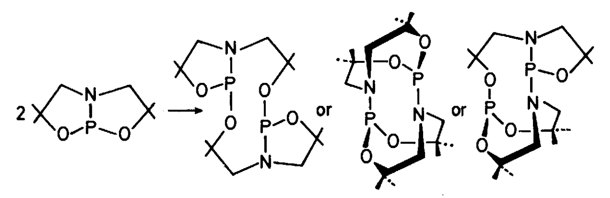
* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.



(1) (2)homo (2)homo (2)hetero

Scheme. The two homo and one hetero dimers which can be obtained by dimerization of (1)

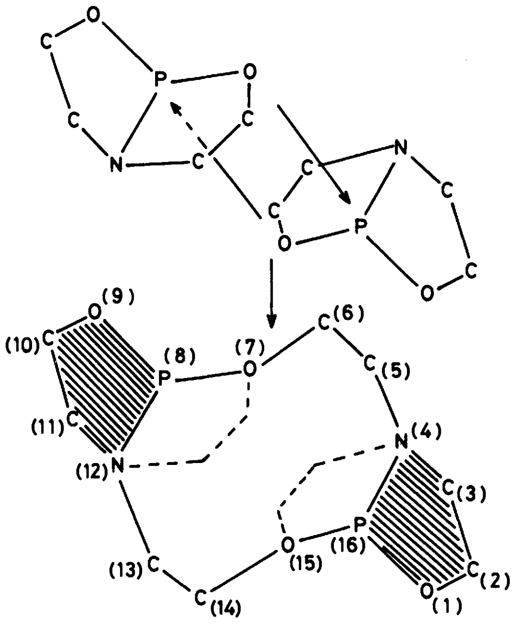
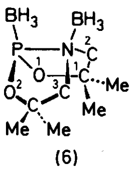


Figure 2. Concerted displacement of oxygen lone pairs and P–O bond electrons in the formation of dimer (2)

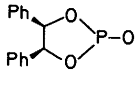
feasible structure with both phosphorus lone pairs ' outside '. In principle, two more possibilities exist (one or both phosphorus lone pairs ' inside ') but would be very strained.* The heterostructural isomer (iii) has three chiral structures corresponding to the three relative positions of the two phosphorus lone pairs (pseudo-cage molecule). The crystal structure establishes unequivocally that there is only one structure: it is the one formed by rupture and reformation of two P–O bonds in which the phosphorus lone pairs are *trans*-antiparallel.

The position of the remaining oxazaphospholane ring in (2) enables us to localize the two starting monomers in their correct relative position when dimerization has occurred (Figure 2). A concerted displacement of the oxygen lone pairs and of the electrons of the P–O bonds without inversion of the phosphorus atom is the simplest scheme which explains the observed structure.

The dimerization can be considered as being closely connected with the redistribution of RO, R_2N, and RS groups around a trico-ordinated phosphorus atom, a phenomenon thoroughly studied in its thermodynamic aspects.[6] For example, Fluck and Van Wazer[7] have shown that the redistribution of phenoxy- and diethylamino-groups between $P(OC_6H_5)_3$ and $P[N(C_2H_5)_2]_3$ leads to larger amounts of $C_6H_5O{\cdot}P[N(C_2H_5)_2]_2$ and $(C_6H_5O)_2P{\cdot}N(C_2H_5)_2$ than those predicted by the statistical law. This result shows that in acyclic compounds the ability of the P–N bond to be broken is, at least, comparable to that of the P–O bond. In the dimerization presented here, the phosphorus–nitrogen bond is not involved in the process, an observation which confirms recent results: in oxazaphospholanes, the dimerization occurs through P–O bond cleavage only and several diazaphospholanes and phosphorinanes do not exhibit oligomerisation at all.[4] These facts underline the big difference in lability presented by the P–N bond between acyclic and cyclic compounds.



(6)



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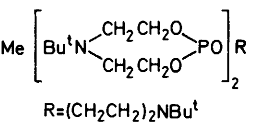
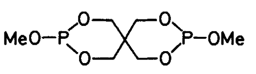


(8)

$(C_6H_5NH)_3P$

(9)



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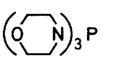

(11)

Table 5. Bond angles around phosphorus and nitrogen atoms of some trico-ordinated phosphorus compounds

Compound	Sum of bond angles around P (°)	Sum of bond angles around N (°)	Reference
(2)	293.72	344.75	This work
(6)	306.6	322.4	8
(7)	296.7		9
(8)	297.1		10
(9)	298.5		11
(10)	302.2		12
(11)	306.6	337.6 353.2 350.5	13

The five-membered ring P(16)–O(1)–C(2)–C(3)–N(4), as well as its crystallographic homologue, adopts a flattened envelope conformation, the C(3) atom being at the top of the fold. It is interesting to notice that in several monomeric bicyclic phosphanes of the same type as (1), analysis of the ^{1}H n.m.r. parameters allows an envelope conformation to be proposed for the oxazaphospholane, the carbon atom linked to oxygen being at the top of the fold.[1] The ten-membered ring formed by the N(4), P(16), O(15), C(14), and C(13) atoms and their crystallographic homologues adopt a boat-chair-boat conformation.

The sum of the bond angles around the phosphorus and nitrogen atoms is, respectively, 293.72 and 344.75°. Although we have never determined the *X*-ray structure of a bicyclic phosphane of type (1), we have carried out a conformational study, assuming that phosphorus and nitrogen are pyramidal.[1] This assumption was confirmed recently [8] by the determination of the crystal structure of the adduct (6) of (1) with two molecules of BH_3, where the sum of bond angles O(1)PO(2), O(1)PN, and O(2)PN is 306.6° and that of bond angles C(2)NC(3), C(2)NP, and C(3)NP is 322.4°. The same parameters in the free bicyclic phosphane (1) should be of the same order or even smaller. It appears clearly that the decrease of the constraint due to the bicyclic structure favours the tendency of the nitrogen atom linked to phosphorus to be planar or nearly planar while the phosphorus atom stays pyramidal. Moreover this phosphorus atom is the most pyr-

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* The structure with only one phosphorus lone pair ' inside ' is chiral.

amidal one among several trico-ordinated phosphorus compounds (7)—(11) whose structures were determined by *X*-ray diffraction, as we can see in Table 5.

Experimental

3,3,7,7-*Tetramethyl*-2,8-*dioxa*-5-*aza*-1-*phospha*$^{\text{III}}$*bicyclo*[3.3.0]*octane* (1) was obtained by following a previously described procedure[14] by treating tris(dimethylamino)phosphane with 1,1,5,5-tetramethyl-3-azapentane-1,5-diol. A xylene solution (100 cm^3) of the phosphane (4.075 g, 25 mmol) and the diol (4.025 g, 25 mmol) was heated during 4 h at 140 °C. The evolved dimethylamine, titrated by a sulphuric acid solution, was 95% of the expected amount. The ^{31}P n.m.r. spectrum of the reaction mixture showed two peaks at δ_1 163 and δ_2 140.8 p.p.m. Evaporation of the solvent led to liquid and solid products. Distillation of the liquid, b.p. 29 °C at 10^{-3} Torr, yielded only a few drops of a non-viscous liquid whose ^{31}P n.m.r. spectrum exhibited only the signal at δ_1 163 p.p.m. The analysis of the ^{1}H n.m.r. spectrum indicated that it was the monomer. The other part of the liquid fraction polymerizes at room temperature. This polymerization is accelerated by heating. The ^{31}P n.m.r. spectrum of the solid, dissolved in benzene, showed only one peak at δ_2 140.8 p.p.m. Recrystallisation in dry xylene gave *crystals* which decompose at 150 °C, *m*/*e* 378 (M^+) (Found: C, 50.9; H, 8.4; N, 7.25; P, 16.3. $C_{16}H_{32}N_2O_4P_2$ requires C, 50.8; H, 8.5; N, 7.4; P, 16.35%).

1,1,5,5-*Tetramethyl*-3-*azapentane*-1,5-*diol* was obtained by the following reaction of 2,2-dimethyloxiran and ammonia. A mixture of 2,2-dimethyloxiran (36 g, 0.5 mol) and NH_4OH (42.5 g, 2.5 mol) was heated in a sealed vial at 100 °C during 15 h. The excess of ammonia is necessary to avoid the formation of $N[CH_2{\cdot}C(CH_3)_2{\cdot}OH]_3$. After evaporation of water, distillation under reduced pressure gave two fractions, one with b.p. 55—60 °C at 10^{-2} Torr corresponding to the aminoalcohol $H_2N{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}OH$ and the other with b.p. 85—90 °C at 10^{-2} Torr corresponding to the expected *aminodiol* (16 g, 40%), m.p. 3 °C, δ_H ($CDCl_3$; 60 MHz) 2.3 (3 H, s, 2 OH + 1 NH), 2.61 (4 H, s, OCH_2), and 1.23 (6 H, s, CH_3) (Found: C, 59.1; H, 11.7; N, 8.8. $C_8H_{19}NO_2$ requires C, 59.6; H, 11.9; N, 8.7%).

Fourier transform ^{31}P and ^{1}H n.m.r. spectra were obtained on Perkin-Elmer R-32 (36.4 MHz) and Varian T60 (60 MHz) instruments respectively. Chemical shifts are given in p.p.m. downfield from 85% H_3PO_4 (^{31}P) and tetramethylsilane (^{1}H). The accuracy is ±0.2 p.p.m. for δ_P and ±0.05 p.p.m. for δ_H. Mass spectra were obtained with a Varian MAT 311 mass spectrometer equipped with a combined e.i.–f.i.–f.d. ion source.

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