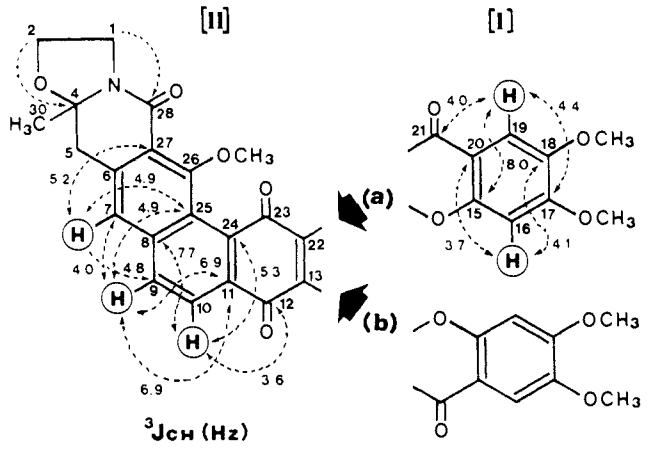
Scheme I



of H-7 in ring C with H-5 in ring B and H-9 in ring D. There are two possibilities, (a) and (b), for the connectivity of I to II as shown in Scheme I. In general, the chemical shift value of a quinone carbonyl carbon (or hydroquinone carbonyl) neighbor to the carbonyl of a γ-pyrone system[4] appears to be deshielded compared with the value when a quinone carbonyl locates to the ether oxygen of a γ-pyrone. The observation of $^4J_{CH}$ = 0.7Hz between H-10 and C-13 (δ 153.6) attached to an ether oxygen in addition to the above chemical shift values (C-12 δ 178.2; C-23, δ 183.2) afforded the validity of the connectivity a. The structures of **2** and **4** were also confirmed from the detailed NMR data of monoacetylcervinomycin A_2 (**6**): mp 283 °C, $[\alpha]^{27}_D$ −297° (*c* 0.32, $CHCl_3$); EIMS, *m/z* 569 (M^+), $C_{31}H_{23}NO_{16}$; UV $\lambda_{max}^{CHCl_3}$ 244 nm (ε 30950), 274 (21400), 307 (25500), 374 (9100), IR ($CHCl_3$): ν_{CO} 1775 cm^{-1}, which was obtained by acetylation of **2** in a similar manner of **3**. Thus, a polycyclic structure containing a xanthone skeleton was assigned for **2**.

The structure of the second methylation product **5** was assigned as the C-7 methylation product from a comparison with the chemical shift values of **4** and the observation of $^3J_{CH}$ of the methyl proton at C-7 with C-6 and C-8. It seems to be quite rare that the C-methylation occurs at the para position of a doubly α,β-substituted phenol derivative with CH_3I in the presence of Ag_2O. The hydroquinone structure of **1** was determined from the fact that acetylation of **1** with $(CH_3CO)_2O$ in pyridine in the presence of $(Et)_3N$ and oxidation of **1** with Ag_2O afforded a triacetate **3** and **2**, respectively.

Only three antibiotics of a xanthone structure have been reported in the literature, lysolipin I, a glycopeptide synthesis inhibitor,[5,6] albofungin (BA-180265, kanchanomycin), and chloroalbofungin, a DNA and RNA synthesis inhibitor.[7,8] As shown in ref 9, the xanthone ring of cervinomycin is identical with that of lysolipin I; however, it is a noteworthly that of albofungin is in an inverted arrangement. We are now investigating the biosynthetic correlation among cervinomycin, lysolipin I, and albofungin by feeding experiment using ^{13}C-labeled precursors.

Acknowledgment. We express our thanks to Hideki Shimizu of the Asahi Chemical Industries, Co., Ltd., for providing cervinomycins A_1 and A_2 samples.

Supplementary Material Available: Complete assignments of ^1H and ^{13}C chemical shifts in 400-MHz NMR are provided for compounds **2** and **4–6** (1 page). Ordering information is given on any current masthead page.

(4) McIness, A. G.; Smith, D. G.; Walter, J. A.; Vining, L. C.; Wright, J. L. C. *J. Chem. Soc., Chem. Commun.* **1975**, 66.
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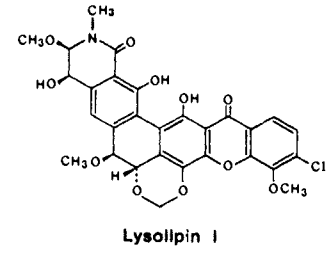
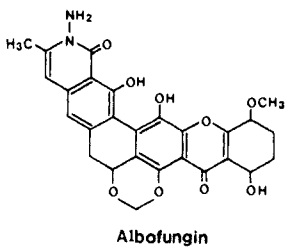
(9) The structures of lysolipin I and albofungin were determined by X-ray analysis and chemical degradation, respectively.


Lysolipin I


Albofungin

Synthesis and Characterization of the First Stable Cyanocyclophosphazenes

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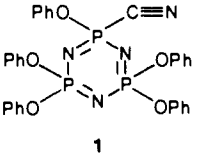
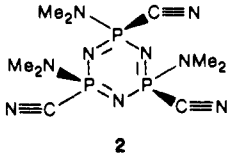
Received May 22, 1986

Cyclic and high polymeric phosphazenes are known that possess a wide variety of inorganic, organometallic, and organic side groups.[1-3] However, until now, no stable cyanophosphazenes have been reported, although attempts have been made to isolate such species.[4,5] Compounds of this type are of considerable interest as substrates for organic synthesis reactions based on the nitrile function, as ligands for transition metals, and as polymerization "monomers". We report here the synthesis and structure determination of the first stable cyanocyclophosphazenes.

Two typical cyanophosphazenes synthesized in this work are shown as **1** and **2**. Species **1** was prepared by the reaction of


1


2

monochloropentaphenoxycyclotriphosphazene, $N_3P_3Cl(OPh)_5$,[6] with potassium cyanide in acetonitrile at 82 °C during 24 h in the presence of tetra-*n*-butylammonium bromide as a phase-transfer agent. The yield was 81%. Anal. Calcd for $C_{31}H_{25}N_4O_5P_3$ (**1**): C, 59.42; H, 3.99;, N, 8.95. Found: C, 59.55; H, 4.24; N, 8.90. Low-resolution mass spectral analysis showed the expected molecular ion at *m/e* 626, and infrared analysis provided evidence for a cyano group stretch at 2200 cm^{-1}. Analysis of the ^{31}P NMR spectrum showed an A_2B spin system (δ_A 5.8, δ_B = −9.2, J_{PNP} = 55 Hz, relative to 85% H_3PO_4). Crystals of **1** were grown by the slow cooling of a warm, saturated solution in hexane, and the molecular structure was confirmed by single-crystal X-ray diffraction analysis. The structure of **1** is shown in Figure 1, and the important molecular dimensions are summarized in Table I.[7]

Species **2** was prepared by the reaction of *trans*-tris(dimethylamino)trichlorocyclotriphosphazene, $[NPCl(NMe_2)]_3$,[8] with potassium cyanide in acetonitrile in the presence of tetra-*n*-butylammonium bromide and traces (0.1%) of water at 82 °C during 10 days. The yield was 5%. Anal. Calcd for $C_9H_{18}N_9P_3$: C,

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(7) X-Ray analysis of **1**: space group $P2_1/n$; unit cell, *a* = 10.759 (4) Å, *b* = 9.662 (3) Å, *c* = 29.466 (4) Å, β = 96.92 (2)°; 5334 unique reflections measured on an Enraf-Nonius CAD4 diffractometer at 293 K; solved by direct and Fourier methods; full-matrix least-squares refinement; hydrogen atoms from difference map at fixed positions; final *R* = 0.045 and R_w = 0.047 for 3238 observed reflections with $I > 3\sigma(I)$.
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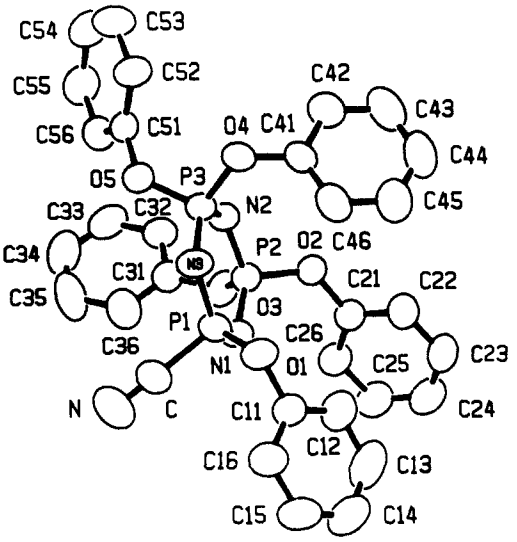

Figure 1. ORTEP representation of the structure of monocyanopentaphenoxycyclotriphosphazene (**1**).

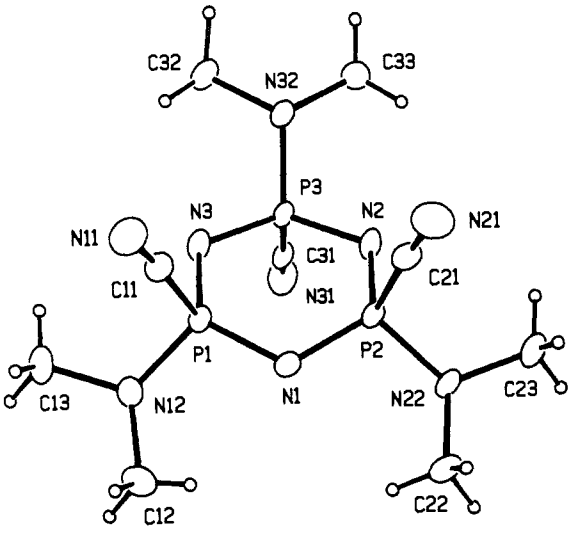

Figure 2. ORTEP representation of the structure of non-*gem*-*trans*-tris(dimethylamino)tricyanocyclotriphosphazene (**2**).

Table I. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

		Compound **1**	
P(1)-N(1)	1.564 (2)	N(1)-P(1)-N(3)	119.3 (1)
P(1)-N(3)	1.567 (2)	N(1)-P(2)-N(2)	117.4 (1)
P(2)-N(1)	1.585 (2)	N(2)-P(3)-N(3)	117.4 (1)
P(2)-N(2)	1.570 (2)	P(1)-N(1)-P(2)	120.9 (1)
P(3)-N(2)	1.574 (2)	P(2)-N(2)-P(3)	122.6 (1)
P(3)-N(3)	1.577 (2)	P(1)-N(3)-P(3)	121.4 (1)
P(1)-C	1.781 (3)	O(2)-P(2)-O(3)	99.6 (1)
C-N	1.134 (3)	O(4)-P(3)-O(5)	100.7 (1)
		O(1)-P(1)-C	101.6 (1)
		P(1)-C-N	177.1 (3)
		Compound **2**	
P(3)-C(31)	1.819 (2)	N(1)-P(1)-N(3)	118.58 (9)
P(2)-C(21)	1.812 (2)	N(1)-P(2)-N(2)	117.86 (8)
P(1)-C(11)	1.815 (2)	N(2)-P(3)-N(3)	119.71 (9)
C(11)-N(11)	1.145 (3)	P(1)-N(1)-P(2)	119.5 (1)
C(21)-N(21)	1.139 (3)	P(2)-N(2)-P(3)	119.6 (1)
C(31)-N(31)	1.145 (3)	P(1)-N(3)-P(3)	119.4 (1)
P(3)-N(32)	1.625 (2)	P(1)-C(11)-N(11)	176.0 (2)
P(2)-N(22)	1.628 (2)	P(2)-C(21)-N(21)	176.3 (2)
P(1)-N(12)	1.623 (2)	P(3)-C(31)-N(31)	176.7 (2)
ring P-N(av)	1.587		

31.30; H, 5.22; N, 36.52. Found: C, 31.34; H, 5.25; N, 36.70. Low-resolution mass spectral analysis showed the expected molecular ion at *m/e* 345. The infrared spectrum contained a cyano stretching peak at 2180 cm^{-1}. The ^{31}P NMR spectrum consisted of a singlet at −7.8 ppm. Crystals suitable for X-ray analysis were grown by slow evaporation of a solution of **2** in hexane. The structure of **2** is illustrated in Figure 2, and important structural parameters are given in Table I.[9]

Both compounds, **1** and **2**, are stable in contact with the atmosphere and are unaffected when heated to moderate temperatures.

The X-ray structural information for both **1** and **2** is consistent with a cyano rather than an isocyano arrangement,[10] and this is confirmed by the infrared spectra.[11] The triple bonds of the cyano groups in **2** are slightly longer than that in **1**, but no evidence could be found for multiple bonding between the cyano groups and the phosphazene ring. The carbon–phosphorus bond lengths are similar to those reported elsewhere for cyano groups attached to phosphorus through single bonds.[12]

Acknowledgment. We thank the U.S. Army Research Office for the support of this work.

(9) X-ray analysis of **2**: space group $P\bar{1}$; unit cell, a = 6.715 (3) Å, b = 8.538 (5) Å, c = 14.910 (6) Å, α = 92.10 (4)°, β = 105.41 (4)°, γ = 95.75 (4)°; 2861 unique reflections measured on an Enraf-Nonius CAD4 diffractometer at 140 K; solved by direct and Fourier methods; full-matrix least-square calculations; hydrogen atoms from difference map and refined isotropically; final R = 0.044 and R_w = 0.061 for 2460 observed reflections $I > 3\sigma(I)$.

(10) Refinement of the three cyano groups in **2** as isocyano units caused the structure to converge with R = 0.058 and R_w = 0.089, significantly higher values than found for the cyano-type arrangement.[9]

(11) For example, see: Seyferth, D.; Kahleen, N. *J. Am. Chem. Soc.* **1960**, *82*, 1080.

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Stereocontrol in Intramolecular Hydrosilation of Allyl and Homoallyl Alcohols: A New Approach to the Stereoselective Synthesis of 1,3-Diol Skeletons[1]

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Received February 10, 1986

We report herein a new methodology for the regio- and stereocontrolled synthesis of 1,3-diols from certain allyl and homoallyl alcohols via intramolecular hydrosilation followed by oxidative cleavage of the carbon–silicon bond.

Much attention has recently been paid to the regio- and stereoselective olefin functionalization through olefin cyclization induced by external[2] or internal[3] electrophiles. Intramolecular hydrometalation, however, has scarcely been studied so far from the viewpoint of regio- and stereocontrol in acyclic systems,[4] despite the potential utilities.

We have now developed an intramolecular hydrosilation as a new promising methodology for such purposes. The intramolecular

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