Synthesis of Dialkyl Phosphorocyanidites. Axial Preference of the *P*-Cyano Group in the 1,3,2-Dioxaphosphorinane Ring System

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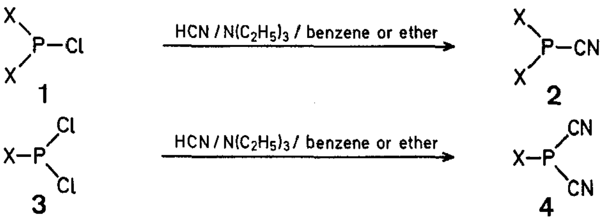
For comparison with the products obtained from the deselenization of *O,O*-dialkylphosphorous isoselenocyanates (dialkyl phosphoroisoselenocyanatidites)[1], we needed dialkyl phosphorocyanidites (**2**, X=OAlk). These compounds have been prepared by Cl/CN exchange of dialkyl phosphorochloridites (**1**, X=OAlk) using metal cyanides [Cu(I), Na, K, Ag][2]. Silver cyanide has been recommended as the most effective reagent, especially when the exchange reaction is carried out in acetonitrile solution[2]. However, ^{31}P-N.M.R. analysis of the product obtained from the reaction of dialkyl phosphorochloridites with silver cyanide has shown that the reaction mixture always contains significant amounts of unreacted starting material; purification of the product may be difficult due to an insufficient difference of boiling points of substrate and product. Another difficulty may arise from possible complexation of silver ions with phosphorus ligands in the case of cyclic dialkyl phosphorochloridites, resulting in the contamination of the reaction product with silver compounds.

We have now found that dialkyl phosphorocyanidites (**2**, X=OAlk) can be prepared in >70% yield and in good purity by reaction of dialkyl phosphorochloridites (**1**, X=OAlk) with hydrogen cyanide in benzene or ether at 0–5° in the presence of triethylamine. ^{31}P-N.M.R. analysis of the products isolated by distillation in vacuo does not show any trace of starting material.

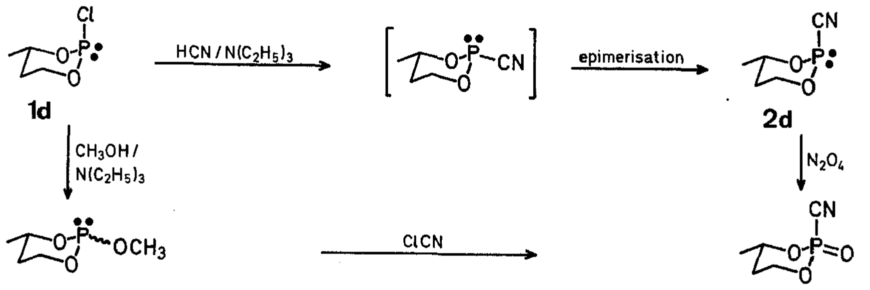
Our procedure is also applicable to the synthesis of cyanodiphenylphosphine (**2**, X=C_6H_5) from chlorodiphenylphosphine (**1**, X=C_6H_5), of alkyl phosphorodicyanidites (**4**, X=OAlk) from alkyl phosphorodichloridites (**3**, X=OAlk), and of dicyanophenylphosphine (**4**, X=C_6H_5) from dichlorophenylphosphine (**3**, X=C_6H_5).



X = Alkyl-O–, C_6H_5

The distilled product **2d** (2-cyano-4-methyl-1,3,2-dioxaphosphorinane) obtained from the *trans*-2-chloro derivative **1d**, exists as a single isomer. Its ^{13}C-N.M.R. spectrum indicates that **2d** has a *trans*-geometry with an equatorial 4-methyl group and an axial 2-cyano group. This conclusion was drawn from the fact that spin-spin coupling between C-5 and P (4.4 Hz) is of an order characteristic of an equatorial-equatorial relationship between the 4-methyl group and the lone pair of electrons at the P-atom[4]. This means that the 2-cyano group on the 1,3,2-dioxaphosphorinane ring prefers the axial orientation as is known for alkyl[5], aryl[6], halogen[7], hydrogen[8], methylthio[9], and alkylamino substituents[10]. The kinetic product of the reaction of *trans*-2-chloro-4-methyl-1,3,2-dioxaphosphorinane with hydrogen cyanide is the *cis* isomer. This has been proved by separate experiments carried out at −30°; the ^{31}P-N.M.R. spectrum recorded immediately after removal of triethylamine hydrochloride showed the presence of two isomers with $\delta = -94.9$ (*cis*) and $\delta = -105.0$ ppm (*trans*) in the ratio 70:30. The spectrum of the same sample recorded after 15 min storage at 37° showed a ratio *cis*:*trans*=10:90. The spectrum of the distilled product has only one signal at −105.0 ppm, characteristic of the thermodynamically more stable *trans* isomer. However, the I.R. spectrum of a freshly prepared sample shows only one absorption characteristic of the CN group. This illustrates the limitation of I.R. spectrometry for detection of geometrical isomerism in the investigated system.

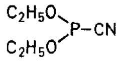
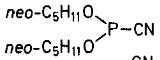
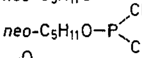
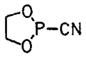
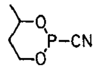
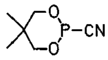
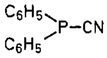
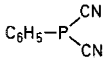
Oxidation of *trans*-**2d** with dinitrogen tetroxide in dichloromethane gave exclusively one compound, 2-cyano-4-methyl-2-oxo-1,3,2-dioxaphosphorinane, (**6**), m.p.=74–75°, $\delta_{^{31}P} = +28.5$ ppm (H_3PO_4). Due to the known stereospecificity of the oxidation of cyclic P^{III} compounds with dinitrogen tetroxide[11], this isomer is assigned the *trans* geometry.



5 *cis*:*trans* = 6 : 94
5′ *cis*:*trans* = 82 : 18

6 *cis*:*trans* = 27 : 73
6′ *cis*:*trans* = 22 : 78

Table. Compounds **2** and **4** prepared.

Product		Yield [%]	b.p. (m.p.)	n_D	I.R. (neat) ν_{CN} [cm^{-1}]	^{31}P-N.M.R. (H_3PO_4) δ [ppm]	References
2a		72	76–78°/25 torr	$n_D^{23} = 1.4242$	2195 (m, sh)	−117.5	2
2b		83	81–82°/4 torr	$n_D^{23} = 1.4337$	2190 (w, sh)	−119.5	—[a]
4b		68	106–108°/32 torr	$n_D^{23} = 1.4550$	2180 (s, sh)	− 22.3	—[a]
2c		71	84–85°/25 torr	$n_D^{28} = 1.4775$	2185 (m, sh)	−115.0	—[a]
2d		79	84–85°/14 torr (m.p. 43–44°)	$n_D^{28} = 1.4616$	2190 (w, sh)	−105.0	—[a]
2e		84	76–77°/8 torr	$n_D^{18} = 1.4670$	2170 (w, sh)	−100.7	1, 14
2f		81	110–112°/0.25 torr	$n_D^{22} = 1.6195$	no CN absorption[b]	+ 35.0	2
4f		76	160–162°/35 torr (m.p. 36–37°)	$n_D^{19} = 1.5815$	2190 (w, sh)	+ 76.2	2

[a] This work.

[b] Compound **2f** prepared according to Ref.[2] can also not be characterized by a CN absorption.

Attempts to synthesize the *cis* isomer by reaction of *trans*-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane (**5**) with cyanogen chloride gave a mixture of both isomers in the ratio 27:73, with $\delta_{^{31}P} = +32.5$ ppm and $\delta_{^{31}P} = +28.5$ ppm (H_3PO_4), respectively. Reaction of the *cis*-2-methoxy derivative with cyanogen chloride gave a mixture with the ratio 22:78. The experiments once again proved the lack of stereospecificity of the Arbusov-type reaction of phosphites with pseudohalogens[12]. In these reactions, the thermodynamically more stable 2-oxo isomers are formed preferentially.

Addition of selenium to *trans*-**2d** gave a mixture of *trans*- and *cis*-2-cyano-4-methyl-2-selenoxo-P^V-1,3,2-dioxaphosphorinanes which was analyzed by ^{31}P-N.M.R. spectrometry [*trans*: 92%, $\delta = -28.2$ ppm, $^1J_{PSe} = 1040$ Hz; *cis*, 8%, $\delta = -23.4$ ppm][13].

Synthesis of Dialkyl Phosphorocyanidites (2); General Procedure: Hydrogen cyanide is introduced into a stirred solution of a dialkyl phosphorochloridite (**1**; 0.1 mol) and triethylamine (0.11 mol) in benzene or ether (200 ml) at 0–5°. Stirring is continued for 30 min at room temperature. Then, triethylamine hydrochloride is filtered off and the solvent is evaporated. The residue is distilled under reduced pressure.

Compounds **4** are obtained in an analogous manner.

All operations have to be carried out in a well-ventilated hood or in a closed vacuum-line system.

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[12] W. J. Stec, M. Mikołajczyk, *Tetrahedron* **29**, 539 (1973).

[13] $^1J_{PSe}$ could not be determined due to the low concentration of the *cis* isomer.

[14] Oxidation of **2e** with dinitrogen tetroxide in dichloromethane gave 2-cyano-5,5-dimethyl-2-oxo-P^V-1,3,2-dioxaphosphorinane: $\delta_{^{31}P} = +28.5$ ppm; m.p. 68–69° [not 79–81°, as erroneously stated in our previous communication: W. J. Stec, A. Konopka, B. Uznański, *J. Chem. Soc. Chem. Commun.* **1974**, 923].