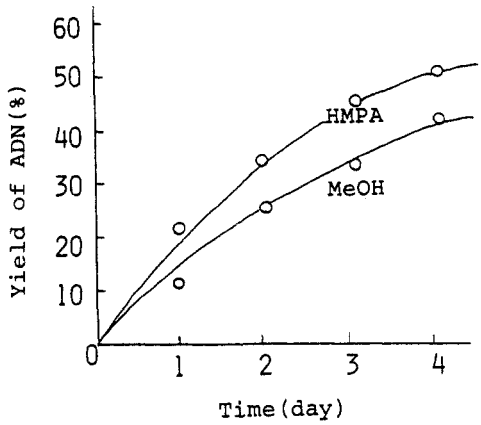


Figure 1. Effect of time on the reduction of acrylonitrile by Zn in the presence of MV^{2+} (20 mol %).

Table I. Reduction of Acrylonitrile (AN) by Zn[a] in the Presence of V^{2+}

V^{2+}[b]	V^{2+}/AN[c] (mol ratio)	recovered AN (%)	yield (%) ADN	yield (%) PrN
MV^{2+}[d]	0.10	64	34	0
	0.05	87.7	12.3	0
	0.02	95	5	0
P-1	0.02	85	15	0
P-2	0.02	88	12	0

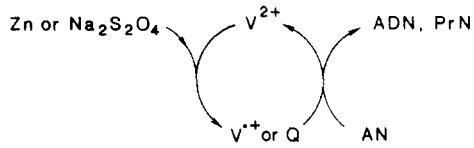
[a] Zn = 60 mmol, AN = 50 mmol, $MeOH/H_2O$ = 5/1, 4 days, 50 °C. Zn/Zn^{2+} ($E°$ = −0.762 vs. SHE). [b] *N,N'*-Dialkyl-4,4'-dipyridinium (V^{2+}). [c] $E_{1/2}$ = −1.94 vs. SCE. [d] $E°$ = −0.44 (pH 7, 30 °C).

Table II. Solvent Effect on Reduction of Acrylonitrile (AN)[a]

solvent	V^{2+}/AN	recovered AN (%)	yield of ADN (%)
$MeOH-H_2O$	0.20	57	43
CH_3CN-H_2O	0.20	77	23
$DMF-H_2O$	0.20	65	35
$HMPA[b]-H_2O$	0.20	48	52

[a] Zn = 30 mmol, AN = 25 mmol, org. sol./H_2O = 5/1, 4 days, 50 °C. [b] Hexamethylphosphoramide.

We attempted to reduce AN in an electron-transfer system containing the reducing agents (Zn, $Na_2S_2O_4$) and V^{2+} as ETC.



The reduction of AN with zinc powder in the presence of V^{2+} as a catalyst proceeded smoothly to obtain ADN selectively which is afforded by one-electron reduction of AN, although the reduction could not occur at all in the absence of V^{2+} due to a large difference of redox potential between V^{2+} and AN. The results are summarized in Table I. As the amount of MV^{2+} as ETC increased, the yield of ADN increased. The soluble viologen polymer (P-1) and cross-linked polymer (P-2) acted as ETC effectively. The solvent effect in the reduction of AN with zinc by use of MV^{2+} (20 mol %) as ETC was examined, as shown in Table II. The cosolvent such as CH_3CN and DMF lowered the yield of ADN. The effect of time on the yield of ADN is shown in Figure 1. The viologen radical cation obtained by the reduction with Zn acted as active species in the reduction to give ADN.

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Table III. Reduction of Acrylonitrile (AN) by $Na_2S_2O_4$ in the Presence of V^{2+}[a]

V^{2+}	V^{2+}/AN (mol ratio)	recovered AN (%)	yield (%) ADN	yield (%) PrN
MV^{2+}	0.10	15	62.5	12.5
	0.05	54.5	30	15.5
	0.02	92.7	2.1	5.2
P-1	0.02	18.6	33.7	47.7
P-2	0.02	34.1	29.3	36.6
quinoid	2.20[b]	5	49.0	46.0

[a] AN = 50 mmol, $Na_2S_2O_4$ = 60 mmol, K_2CO_3 = 100 mmol, $MeOH/H_2O$ = 1/1, 4 days, rt, under argon. [b] Quinoid as reducing agent.

Reduction of Acrylonitrile with $Na_2S_2O_4/V^{2+}$ System. It has been reported[8,10] that viologen derivatives give the quinoid form (Q) by two-electron reduction with sodium dithionite ($Na_2S_2O_4$) in alkaline solution. It was found that AN was reduced with $Na_2S_2O_4$ in the presence of V^{2+} as an ETC to ADN and PrN. Both radical cation and quinoid form were active species in the reduction, and 1,1'-dihydrodipyridyl (Q), which was obtained by the reduction of MV^{2+} with $Na_2S_2O_4$, could easily reduce AN to give ADN and PrN as shown in Table III. Further, fumaronitrile as a substrate could be also reduced by Zn or $Na_2S_2O_4$ with MV^{2+} to obtain succinonitrile quantitatively. Our results suggest that V^{2+} such as MV^{2+} and polymeric viologen have played the role of catalysts for the reduction of active olefines, and especially AN is reduced to ADN or PrN by the difference of reducing agents.

Registry No. Q, 25128-26-1; MV^{2+}, 1910-42-5; AN, 107-13-1; ADN, 111-69-3; PrN, 107-12-0; Zn, 7440-66-6; sodium dithionite, 7775-14-6.

The Structure of Two Isomeric 1,3,2-Dioxaphosphorinanes

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Previously,[1] we have reported the synthesis of 5-(benzyloxy)-2-chloro-1,3,2-dioxaphosphacyclohexane 2-oxide (**1**) which was used to prepare 2'-deoxy-5-fluoro-5''-hydroxy-5'-*O*-1'',3'',2''-dioxaphosphacyclohex-2''-yluridine 2''-dioxide (**2**). At the time, we commented on the fact that these compounds could exist in two isomeric forms, depending upon the orientation of the substituent in the 1,3,2-dioxaphosphacyclohexane ring, but we could not establish the orientation or indeed whether they were mixtures. We subsequently became aware of a paper by Denney and Varga[2] in which they reported the synthesis of 5-hydroxy-2-methoxy-1,3,2-dioxaphosphacyclohexane 2-oxide (**3**), but again the configuration was not established, although they suspected that the isomer with the methoxyl and hydroxyl groups in the axial positions was the most likely one to be present.

Our interest in the synthesis of **2** was a part of a project to prepare metabolically labile[3] and acid-labile dioxap-

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(3) Hunston, R. N.; Jehangir, M.; Jones, A. S.; Walker, R. T. *Tetrahedron* **1980**, *36*, 2337.

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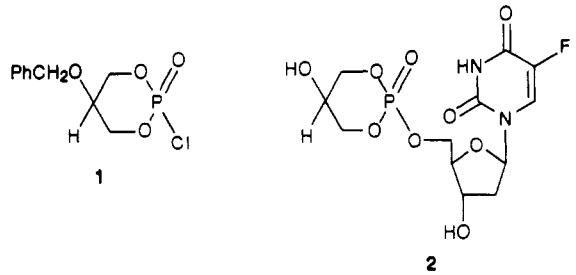
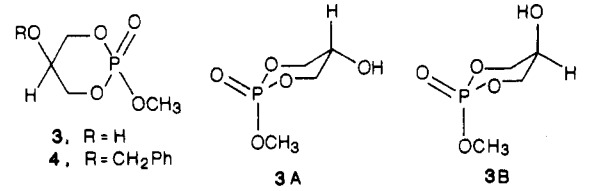
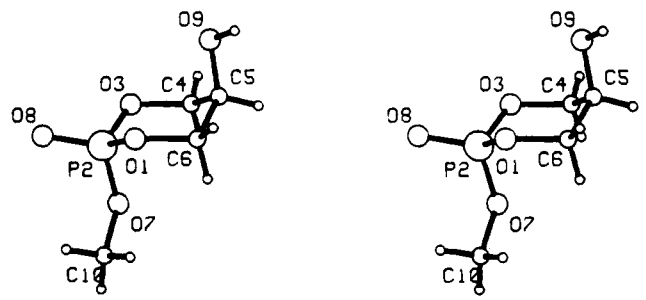




hospha and oxazaphospha heterocycles,[1,4] which under physiological conditions would yield the nucleoside monophosphate once the cyclic phosphotriester had penetrated the cell wall. This approach has also recently been reported by others.[5] Our derivative **2** was far too stable, and it occurred to us that if the compound reported by Denney and Varga had indeed the stereochemistry they suspected and if the corresponding nucleoside derivative were synthesized and it proved to be different from that previously reported by us,[1] it might be more labile because of the possibility of neighboring group participation by the axial hydroxyl group of the 1,3,2-dioxaphosphacyclohexane ring.

We thus prepared compound **3** first by a modification of the method previously described by us[1] from 2-*O*-benzylglycerol to give **3A** and second by the method described by Denney and Varga[2] to give **3B**. The proton NMR spectra of **3A** and **3B** were recorded at 270 MHz and ^{31}P spectra at 162 MHz with proton decoupling. The spectra from preparation **3B** clearly show that the hydroxyl group is in the axial position and the H-5 in the equatorial position is found upfield as would be expected. The axial H-4 and H-6 protons are also clearly seen downfield from the equatorial H-4 and H-6 protons. The identity of this isomer (**3B**) was confirmed by X-ray analysis (see stereo diagram).[10]



The proton NMR spectrum of the product from preparation **3A** is much more complex and difficult to interpret. However the signal due to the H-5 axial proton is 0.2 ppm downfield when compared with the corresponding signal from the other isomer, and this effect has been seen before.[6] As the other isomer can be unequivocally identified as having structure **3B**, this isomer, prepared from 2-*O*-benzylglycerol must be and has the properties expected for structure **3A**.

Compounds **3A** and **3B** were used as model compounds to determine the lability of the dioxaphosphacyclohexane ring. Under physiological conditions both were stable, and it required 0.2 M HCl under reflux before any appreciable hydrolysis could be achieved. Under these conditions the half lives were as follows: **3A**, 2 h; **3B**, 5 h. At pH 10.6 at room temperature, the corresponding values were as follows: **3A**, 1 h; **3B**, 4 h.

Experimental Section

Synthesis of 4. Methyl phosphorodichloridate[7] (2.25 g, 15 mmol) was added to a solution of 2-*O*-benzylglycerol[8] (2.74 g, 15 mmol) and 2,6-lutidine (3.48 mL, 30 mmol) in dry benzene. After 18 h at room temperature, the mixture was filtered and the filtrate reduced to an oil which was dissolved in chloroform and fractioned on a silica column using ethanol/chloroform (5:95). The crude product was crystallized from benzene/cyclohexane (yield 1.9 g, 49%):[9] mp 66–68 °C; ^1H NMR ($CDCl_3$) δ 7.35 (5 H, s, Ph), 4.62 (2 H, s, $PhCH_2$), 4.33 (5 H, m, H-4, H-5, H-6), 3.87 (3 H, d, CH_3, J_{P-CH_3} = 12 Hz).

Synthesis of 3A. Compound **4** was debenzylated by treatment with 5% Pd/C and hydrogen in dry ethanol at atmospheric pressure and room temperature. Recrystallization of the product from toluene/petroleum ether gave the pure product (yield 45%):[9] mp 79–80 °C; ^1H NMR [$(CD_3)_2SO$] δ 5.6 (1 H, s, OH), 4.4–4.25 (2 H, m, H-4, H-6 axial), 4.02–3.9 (3 H, m, H-6, H-5, and H-4 equatorial), 3.7 (3 H, d, OCH_3, J_{P-OCH_3} = 11 Hz); ^{13}C NMR [$(CD_3)_2SO$] 71.8 (OCH_3), 61 (C_5OH), 54 (CH_2) ppm; ^{31}P NMR [$(CD_3)_2SO$] –5.1; MS, *m/e* 169, 168 (M^+), 95 (base peak), 136, 127, 110.

Synthesis of 3B. This compound was prepared exactly as described by Denney and Varga:[2] mp 111–112 °C;[9] ^1H NMR [$(CD_3)_2SO$] δ 5.6 (1 H, s, OH), 4.4 (2 H, m, H-4 and H-6 axial), 4.2 (2 H, m, H-4 and H-6 equatorial), 3.78 (1 H, m, H-5 equatorial), 3.68 (3 H, d, OCH_3, J_{P-OCH_3} = 11 Hz); ^{13}C NMR [$(CD_3)_2SO$] ppm, 73.4 (OCH_3), 62 (C_5OH), 53 (CH_2); ^{31}P NMR [$(CD_3)_2SO$] –6.8; MS, *m/e* 169, 168 (M^+), 95 (base peak), 140, 127, 110, 79.

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(9) Analytical data for the new compounds described here are in agreement with the assigned structures.
(10) The product **3B** crystals are orthorhombic, space group $Pna2_1$ with a = 10.825 Å, b = 9.342 Å, and c = 6.839 Å. The discrepancy R = 0.035 for 642 reflections.

Estimating Heats of Sublimation of Hydrocarbons. A Semiempirical Approach

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Numerous conceptual models in organic chemistry such as strain and resonance energies implicitly reference the

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