

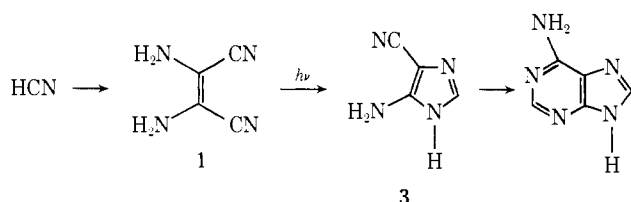
A Quantitative Investigation of the Photochemical Conversion of Diaminomaleonitrile to Diaminofumaronitrile and 4-Amino-5-cyanoimidazole¹

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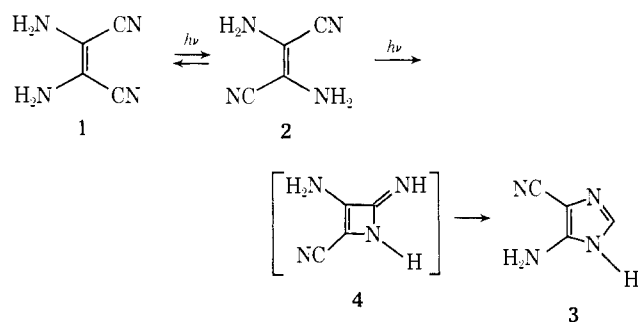
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Abstract: Diaminomaleonitrile (**1**) photochemically isomerizes to diaminofumaronitrile (**2**) with a quantum yield of 0.045. When irradiated through Pyrex with RPR-3000 A lamps, **1** forms a photostationary ratio with **2** which is approximately 20% **1**:80% **2**. Irradiation of the diaminomaleonitrile/diaminofumaronitrile photostationary ratio results in the formation of 4-amino-5-cyanoimidazole (**3**) with a quantum yield of 0.0034. Evidence is presented which shows that the photoreaction leading to **3** is unimolecular, its efficiency is independent of light intensity, and it occurs *via* electronically excited diaminofumaronitrile.

Ferris and Orgel² have reported that irradiation of HCN tetramer (**1**), diaminomaleonitrile, with lamps with maximum emission at 350 nm resulted in a rearrangement to 4-amino-5-cyanoimidazole (**3**). Reac-



tion of **3** with HCN in a dark reaction has been shown to yield adenine. These reactions were proposed as the most plausible route to adenine from HCN under prebiotic conditions. Both Ferris³ and Yamada⁴ have shown that diaminomaleonitrile (**1**) also photochemically isomerizes to diaminofumaronitrile (**2**). The isomerization to **2** occurred more efficiently than the rearrangement to 4-amino-5-cyanoimidazole (**3**). Diaminofumaronitrile (**2**) was proposed as a possible intermediate in the formation of **3** from **1**.⁴ Ferris and Kuder⁵ have also proposed an azetine (**4**) as a possible



intermediate in the rearrangement of **1** to **3**. Becker and coworkers⁶ recently conducted a wavelength study of the excitation of diaminofumaronitrile (**2**) and diaminomaleonitrile (**1**) to establish if **2** was an inter-

mediate in the rearrangement of **1** to **3**. They concluded that either (a) diaminofumaronitrile (**2**) cannot form 4-amino-5-cyanoimidazole (**3**) but can be converted into diaminomaleonitrile (**1**) which can form **3** or (b) there is a wavelength dependence for the formation of **3** from **2**.

We decided that a careful study of the quantum efficiency of formation of diaminofumaronitrile and 4-amino-5-cyanoimidazole as a function of reaction conditions might provide additional evidence regarding the mechanism of this unusual photochemical rearrangement.

Results

Quantum efficiency experiments were performed with a rotating wheel mounted in a Rayonet reactor equipped with RPR-3000 A lamps. Samples were prepared in methanol solvent in the concentration range 1×10^{-3} to 3×10^{-3} M and were freeze-thaw degassed. The light intensity was monitored with potassium ferrioxalate actinometry, and under these experimental conditions the amount of light absorbed as a function of time was constant. Concentrations of **1**, **2**, and **3** were measured by uv absorption.

With this experimental technique the following results were obtained. (a) Diaminomaleonitrile (**1**) isomerizes to diaminofumaronitrile (**2**) with a quantum yield of 0.045 for low conversion. (b) Diaminomaleonitrile (**1**) forms a photostationary ratio (psr) with diaminofumaronitrile (**2**) which is 20% **1**:80% **2**. (c) The photostationary **1**:**2** ratio rearranges to 4-amino-5-cyanoimidazole (**3**) with a quantum yield of 0.0034. (d) The efficiency of formation of **3** as a function of initial diaminomaleonitrile concentration shows an inverse concentration dependence as shown in Table I. (e) The efficiency of formation of 4-amino-5-cyanoimidazole (**3**) as a function of the **1**:**2** photostationary ratio concentration is independent of concentration (Table I). (f) The efficiency of formation of **3** starting with **1** is time dependent as shown in Table II and Figure 1. (g) The efficiency of formation of 4-amino-5-cyanoimidazole (**3**) from the **1**:**2** photostationary ratio is time independent (Table II and Figure 1). (h) The efficiency of formation of **3** starting with diaminomaleonitrile (**1**) is independent of light intensity over the intensity range 0.7×10^{15} to 2.9×10^{15} quanta/sec.

(1) This work was supported by Grant GM 18349 from the National Institutes of Health.

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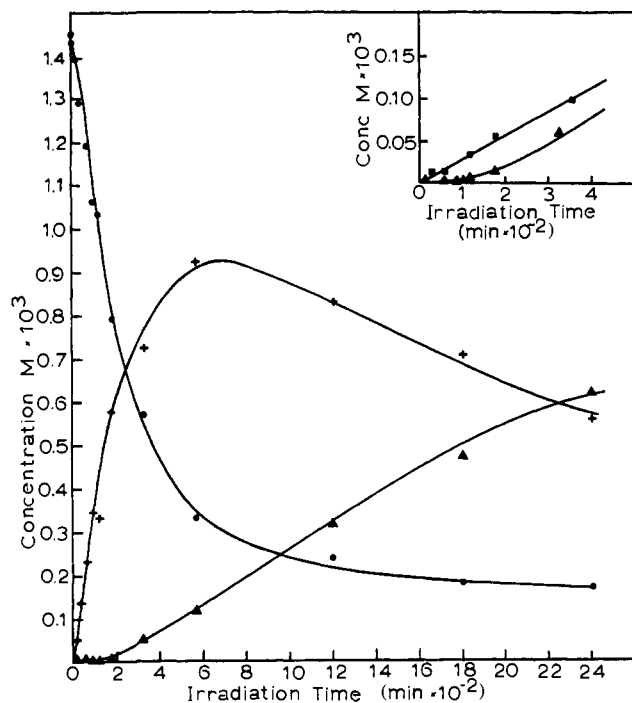


Figure 1. Formation of diaminofumaronitrile (2) and 4-amino-5-cyanoimidazole (3) as a function of time: ●, destruction of 1; +, formation of 2; ▲, formation of 3 from the irradiation of 1; ■, formation of 3 from the irradiation of the 1:2 photostationary ratio, least-squares slope $2.36 \times 10^{-7} \pm 0.10 \times 10^{-7}$ mol/(l. min).

Table I. Formation of 4-Amino-5-cyanoimidazole (3) as a Function of Concentration^a

Irradiation of 1				Irradiation of 1:2 photostationary ratio (psr)	
Initial ($\times 10^3$) [1]	Terminal ($\times 10^3$)		Initial ($\times 10^3$) [1:2 psr]	Terminal ($\times 10^3$) [3]	
	[1]	[2]		[1]	[3]
1.0	0.21	0.66	1.0	0.130	
1.2	0.28	0.74	1.2	0.129	
1.35	0.37	0.82	1.35	0.136	
1.5	0.45	0.94	1.5	0.135	
1.7	0.53	1.01	1.7	0.127	
1.85	0.65	1.05	1.85	0.124	
2.0	0.74	1.16	2.0	0.119	
2.2	0.93	1.17	2.2	0.129	
2.4	1.08	1.13	2.4	0.125	
2.55	1.23	1.11	2.55	0.122	
2.7	1.33	1.24	2.7	0.131	

^a Concentrations are given in mol/l. Concentrations of photo-products are directly proportional to the quantum efficiencies of product formation.

Discussion

Initially we suspected that the photochemical rearrangement of diaminomaleonitrile (1) to 4-amino-5-cyanoimidazole (3) might involve a bimolecular step. This suspicion was based upon Becker's conclusion that diaminofumaronitrile (2) might not be an intermediate. If 2 is not an intermediate, it would be difficult to form Ferris' azetine intermediate (4) directly from 1 in a unimolecular reaction. The fact that the efficiency of formation of 3 was independent of the 1:2 photostationary ratio concentration (Table I), however, established that the reaction is in fact unimolecular.

Table II. Formation of Diaminofumaronitrile (2) and 4-Amino-5-cyanoimidazole (3) as a Function of Time^a

Time, min	Terminal from $h\nu$ 1 ($\times 10^3$) [1]	Terminal from $h\nu$ 1 ($\times 10^3$) [2]	Terminal from $h\nu$ 1 ($\times 10^3$) [3]	Terminal from $h\nu$ psr ($\times 10^3$) [3]	Terminal from $h\nu$ 2 ($\times 10^3$) [3]
0	1.45	0	0	0	0
5	1.43	0.018	0.001		
15	1.39	0.052	0.005		
30				0.010	0.007
60	1.19	0.231	0.004	0.012	0.016
90	1.06	0.344	0.002		
120	1.03	0.331	0.006	0.030	0.031
180	0.79	0.574	0.010	0.049	0.053
330	0.57	0.725	0.053		
360				0.084	0.110
570	0.33	0.921	0.115		
1200	0.24	0.824	0.318		
1800	0.18	0.706	0.473		
2400	0.17	0.558	0.617		

^a Concentrations are given in mol/l. Concentrations of photo-products are directly proportional to the quantum efficiencies of product formation.

The efficiency of 4-amino-5-cyanoimidazole (3) formation for low conversion was inversely related to the initial diaminomaleonitrile (1) concentration (Table I). This result is consistent with diaminofumaronitrile (2) as an intermediate in the conversion of 1 to 3 because at higher initial diaminomaleonitrile (1) concentrations more quanta would be required to produce sufficient 2 to compete efficiently with 1 for light.

The involvement of excited 2 in the formation of 3 was unambiguously established by examining the efficiency of formation of 4-amino-5-cyanoimidazole (3) as a function of time starting with both 1 and the 1:2 photostationary ratio. As shown in Table II and Figure 1, the irradiation of diaminomaleonitrile (1) resulted in the immediate formation of diaminofumaronitrile (2); however, there was a time lag for the formation of 3. The absorption curves for short irradiation times formed a sharp isosbestic point at 317 nm consistent with cis-trans isomerization without rearrangement to 3. A broad isosbestic point at 267 nm was formed by the absorption curves for longer irradiation times. This isosbestic point resulted from formation of 3 and was broad because the 1:2 photostationary ratio had not been reached during the time of the experiment. This time dependence in itself only proved that an intermediate was produced which gave 4-amino-5-cyanoimidazole (3) in a subsequent photoreaction. The fact that 2 was the intermediate was established by the observation that when the 1:2 photostationary ratio was irradiated there was no time lag for the formation of 3 (Figure 1, Table II) and the efficiency of 4-amino-5-cyanoimidazole formation was time independent [least-squares slope, $2.36 \times 10^{-7} \pm 0.10 \times 10^{-7}$ mol/(l. min)]. The intermediacy of diaminofumaronitrile (2) is further confirmed by the fact that there was also no time lag for the formation of 3 starting with 2 and that on the average the efficiency of formation of 3 was a little higher starting with 2 than starting with the 1:2 photostationary ratio (see Table II).

Both Ferris⁵ and Becker⁶ have proposed that there is an intermediate such as the azetine 4 in addition to 2 in the photorearrangement ultimately leading to 3. The conversion of this intermediate to 4-amino-5-cyanoimidazole (3) may or may not be a photochemical reac-

tion. We decided that if the intermediate rearranged to **3** in a photochemical reaction, the existence of the intermediate might be evident from a measurement of the efficiency of formation of **3** as a function of light intensity. Over the light intensity range 0.7×10^{15} to 2.9×10^{15} quanta/sec the efficiency of formation of **3** starting with diaminomaleonitrile (**1**) was constant. This result is not inconsistent with a photochemical rearrangement of an intermediate, but if an intermediate such as **4** is formed from excited **2**, this intermediate must not thermally revert to **1** or **2** in competition with light absorption.

In summary we have shown that for the photochemical rearrangement of diaminomaleonitrile to 4-amino-5-cyanoimidazole, diaminofumaronitrile is an intermediate and the reaction does not involve a bimolecular step. Furthermore, if the conclusion of Becker and coworkers⁶ based on a wavelength study of the excitation of diaminofumaronitrile is correct, then the photorearrangement of diaminofumaronitrile to 4-amino-5-cyanoimidazole is wavelength dependent.

Experimental Section

Preparation and Purification of Reagents. Diaminomaleonitrile (**1**) (PCR, Inc.) was sublimed at 140° (1×10^{-3} mm) and recrystallized from isobutyl alcohol solvent to give white crystals, mp $188\text{--}188.5^\circ$ (lit. mp $181\text{--}183^\circ$).⁷ Diaminofumaronitrile (**2**) was prepared by photochemical isomerization of **1** as described by Yamada and coworkers, mp $169\text{--}170^\circ$ (lit. mp 169°).⁴ 4-Amino-5-cyanoimidazole (mp $126\text{--}128^\circ$, lit. mp $123\text{--}125^\circ$)⁸ was prepared by irradiation of **1** in methanol solvent with a 450-W mercury lamp through a Pyrex filter.² Reagent grade methanol (Fisher) was used as the solvent for all the photochemical experiments without further purification.

Quantitative Measurements. Quantitative photochemical experiments were performed in a Rayonet photochemical reactor Model RPR-100 using RPR-3000 A lamps. The Rayonet reactor was equipped with a rotating wheel and thermostated at $30 \pm 1^\circ$ with a water-cooled heat exchanger as previously described.⁹ Calibration of the compartments of the wheel with potassium ferrioxalate actinometry¹⁰ demonstrated that each compartment of the wheel received identical quantities of light ($\pm 1\%$). Samples for irradiation were 3.0 ml in volume and were prepared in 13-mm Pyrex tubes. All samples were degassed by four freeze (liquid nitrogen)-pump (10^{-5} Torr)-thaw cycles and sealed. Analysis of cis-trans isomerization of **1** and formation of 4-amino-5-cyanoimidazole was performed by uv absorption using a Cary 17 uv-visible spectrophotometer. The concentrations of **1**, **2**, and **3** were calculated from uv absorbances at wavelengths 298 (λ_{max} of **1** (ϵ 14,000)), 313 (λ_{max} of **2** (ϵ 8500)), and 250 nm (λ_{max} of **3** (ϵ 10,700)) using the following equations. Let

$$R_1 = \frac{\text{absorbance of } \mathbf{1} \text{ at } 298 \text{ nm}}{\text{absorbance of } \mathbf{1} \text{ at } 313 \text{ nm}}$$

$$R_2 = \frac{\text{absorbance of } \mathbf{2} \text{ at } 313 \text{ nm}}{\text{absorbance of } \mathbf{2} \text{ at } 298 \text{ nm}}$$

$$A_1 = \text{total absorbance of the unknown mixture at } 298 \text{ nm}$$

$$A_2 = \text{total absorbance of the unknown mixture at } 313 \text{ nm}$$

$$a = \text{absorbance of } \mathbf{1} \text{ at } 298 \text{ nm in the unknown mixture}$$

$$b = \text{absorbance of } \mathbf{2} \text{ at } 298 \text{ nm in the unknown mixture}$$

$$c = \text{absorbance of } \mathbf{2} \text{ at } 313 \text{ nm in the unknown mixture}$$

$$d = \text{absorbance of } \mathbf{1} \text{ at } 313 \text{ nm in the unknown mixture}$$

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Then

$$a + b = A_1 \quad d = \frac{R_2 A_1 - A_2}{R_1 R_2 - 1} \quad a = A_1 - b$$

$$c + d = A_2$$

$$a/d = R_1 \quad b = \frac{R_1 A_2 - A_1}{R_1 R_2 - 1} \quad c = A_2 - d$$

$$c/b = R_2$$

Further let

$$R_3 = \frac{\text{absorbance of } \mathbf{1} \text{ at } 250 \text{ nm}}{\text{absorbance of } \mathbf{1} \text{ at } 298 \text{ nm}}$$

$$R_4 = \frac{\text{absorbance of } \mathbf{2} \text{ at } 250 \text{ nm}}{\text{absorbance of } \mathbf{2} \text{ at } 313 \text{ nm}}$$

$$A_3 = \text{total absorbance of the unknown mixture at } 250 \text{ nm}$$

$$x = \text{absorbance of } \mathbf{3} \text{ at } 250 \text{ nm in the unknown mixture}$$

Then

$$x = A_3 - (R_3 a + R_4 c)$$

From the measurable quantities, R_1 , R_2 , R_3 , R_4 , A_1 , A_2 , and A_3 , the absorbances a , c , and x were calculated. Concentrations were obtained using the observed extinction coefficients. The validity of the analytical technique was verified by preparing solutions with known concentrations of **1**, **2**, and **3** so as to duplicate results obtained in two separate photochemical experiments. The error in duplication was less than 2%.

Formation of 4-Amino-5-cyanoimidazole (3**) as a Function of the Concentration of Diaminomaleonitrile (**1**) and as a Function of the Concentration of a Diaminomaleonitrile/Diaminofumaronitrile Photostationary Ratio.** Diaminomaleonitrile (0.0370 g) was dissolved in 100.0 ml of methanol. To eleven 10-ml volumetric flasks were added the following quantities of the stock solution: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, and 8.0 ml. These were diluted to 10.0 ml and were then irradiated as 3.0-ml samples in the rotating wheel for 8 hr. Uv analysis gave the concentrations of **1**, **2**, and **3** as shown in Table I. The experiment was repeated with a 100.0 ml of methanol, stock solution containing 0.0300 g of **2** and 0.0060 g of **1**. With this mixture the 1:2 ratio did not change after 8 hr of irradiation as evidenced by an initial and terminal uv maximum at 306 nm. As a result the photostationary ratio was assumed to be about 20% **1**:80% **2** under these irradiation conditions. The concentrations of **3** at the end of the irradiation of the various concentrations of the photostationary ratio are also reported in Table I.

Formation of 4-Amino-5-cyanoimidazole (3**) and Diaminofumaronitrile (**2**) as a Function of Time.** Eleven 3.0-ml samples of 1.4×10^{-3} M **1** were prepared and degassed. These were irradiated simultaneously in the wheel and the samples were removed at the various times indicated in Table II. The concentrations of **1**, **2**, and **3** were then measured by uv absorption and are reported in Table II. The uv curves for the samples irradiated between 5 and 180 min formed a sharp isosbestic point at 317 nm and the uv curves for samples irradiated between 570 and 2400 min formed a broad isosbestic point at 267 nm. Similarly five samples, 1.1×10^{-3} M **2** and 0.3×10^{-3} M **1**, were prepared. These samples were also irradiated simultaneously in the wheel for the various times shown in Table II and the concentrations of **3** were measured by uv absorption. The mixture of **2** and **1** irradiated in the latter experiment was the photostationary ratio mixture and no change in the 1:2 ratio occurred. In an analogous experiment five samples of 1.4×10^{-3} M diaminofumaronitrile were prepared, degassed, irradiated in the wheel for the times shown in Table II, and analyzed by uv absorption.

Formation of 4-Amino-5-cyanoimidazole (3**) as a Function of Light Intensity.** Nine 3.0-ml samples of 1.4×10^{-3} M **1** were prepared and degassed. Three of the samples were irradiated simultaneously for 500 min with a light intensity of 2.94×10^{15} quanta/sec as measured by potassium ferrioxalate actinometry. Similarly three samples were irradiated for 1000 min with a light intensity of 1.46×10^{15} quanta/sec, and three samples, for 2200 min with a light intensity of 0.67×10^{15} quanta/sec. Under these conditions each set of three samples received approximately the same number of quanta. When the samples were analyzed in the uv, the average concentrations of **3** were 0.13×10^{-3} , 0.12×10^{-3} , and 0.12×10^{-3} M for the light intensities 2.94, 1.46, and 0.67×10^{15} quanta/sec, respectively.

Quantum Yield of Formation of Diaminofumaronitrile (2) from Diaminomaleonitrile (1) and of 4-Amino-5-cyanoimidazole (3) from the 1:2 Photostationary Ratio. A 3.0-ml sample of $1.4 \times 10^{-3} M$ **1** was prepared, degassed, and irradiated in the wheel for 60 min. The light intensity during the irradiation averaged 2.7×10^{15} quanta/sec as measured by potassium ferrioxalate actinometry. Uv analysis indicated that the concentration of **2** was $1.9 \times 10^{-4} M$, a 14% conversion. This gave a quantum yield of cis-trans isomerization of 0.045 after correction for back reaction¹¹ and after

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correction for the difference in the amount of light absorbed by the actinometer and the amount of light absorbed by **1**. Of the light absorbed by the actinometer, 84% was absorbed by **1**. This percentage was calculated from the uv absorption for the Pyrex glass of the samples tubes, the uv absorption of **1**, the uv absorption of the actinometer, and the lamp emission intensity as a function of wavelength available from the Southern New England Ultraviolet Co., Middletown, Conn. A 3.0-ml solution of $1.1 \times 10^{-3} M$ **2** and $0.3 \times 10^{-3} M$ **1** was similarly irradiated for 476 min. This yielded a concentration of **3** of $1.2 \times 10^{-4} M$ (a 9% conversion) and gave a corrected quantum yield of **3** formation equal to 0.0034.

Monomeric Methyl Metaphosphate¹

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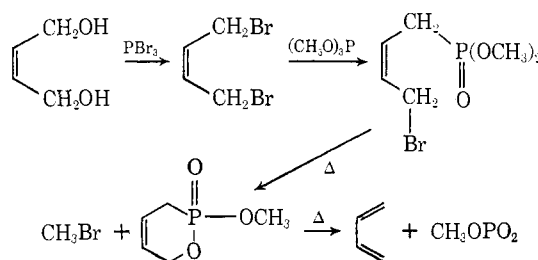
Abstract: Monomeric metaphosphates have been implicated in phosphorylation reactions and in the solvolysis of phosphate esters but none had previously been prepared. In this article, we present evidence that monomeric metaphosphate has been produced in the gas phase by the pyrolysis of methyl 2-butenylphosphonate and trapped by *N*-methylaniline: methyl 2-butenylphosphonate \rightarrow $H_2C=CH-CH=CH_2 + CH_3OPO_2$; $CH_3OPO_2 + 2C_6H_5-NHCH_3 \rightarrow CH_3OP(N(CH_3)C_6H_5)O_2^- + C_6H_5N^+H_2CH_3$.

Monomeric metaphosphate ion, PO_3^- , and esters of monomeric metaphosphoric acid have been postulated as intermediates in numerous phosphorylation reactions,²⁻⁴ in the hydrolysis of monoesters of phosphoric acid,⁵⁻⁷ and in the hydrolysis of various esters of pyrophosphoric acid.⁸ But although trimeric and polymeric metaphosphates are well known,⁹ no salts or esters of monomeric metaphosphoric acid, HPO_3 , have previously been reported. In the present paper, we present experimental evidence for the preparation of monomeric methyl metaphosphate and for trapping it as its methylanilide.

The chemistry of phosphate esters can be compared to that of carboxylic esters. Most reactions occur by nucleophilic attack on the central atom, to form a tetrahedral intermediate from carboxylic esters or a

pentacovalent intermediate from phosphate esters;¹⁰⁻¹² the stereochemistry and ligand reorganization^{10,11} of the latter intermediates have proved complex and these complexities have helped elucidate the detailed mechanism of some of these hydrolytic processes.¹³ But just as carboxylic esters can undergo hydrolysis through acylonium ions, where the ligand number at carbon is reduced from three to two, so some phosphates are presumed to react by way of monomeric metaphosphates, where the ligand number at phosphorus is reduced from four to three. But since monomeric metaphosphate ion is isoelectronic with SO_3 , it might reasonably function as a strong electrophile and therefore be difficult to prepare in solution. (The resonance stabilization that characterizes NO_3^- will be expected to be less prominent in compounds of second-row elements, where double bonding is poorer than with first-row elements.)

A preparation of monomeric methyl metaphosphate from methyl 2-butenylphosphonate by pyrolysis in the gas phase is outlined below.



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