monium halides (Eastman) by treatment of aqueous solutions of the salts with powdered silver oxide. Purines were obtained from commercial sources and used without further purification.

Alkylpurines.—The compounds were prepared as described for 9-methylkinetin (IIIb). Reaction time and temperature as well as recrystallization solvent are given in Table I. Physical constants and analysis of the products are given in Table II.

9-Methylkinetin.—A solution of 0.22 g. (2.38 mmoles) of tetramethylammonium hydroxide (IIa) and 0.50 g. (2.32 mmoles) of kinetin (Ib) in 5 ml. of water was lyophilized. The hydroscopic residue, in a sublimation apparatus, was heated slowly under oil pump vacuum (*ca.* 0.05 mm.) to a temperature of 190–200°. At this temperature a sublimate began to collect on the condenser. After 5 hr. 0.38 g. of sublimed product was collected. An additional 0.07 g. of product was collected on continued heating at 200°. The combined sublimates yielded 0.45 g. (85%) of crude product. A portion of the crude product was recrystallized twice from acetone to give white crystals, m.p. 176.5–177.5°, undepressed when admixed with an authentic sample of 9-methylkinetin.[8]

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(12) Melting points were taken on a Kofler hot-stage microscope and are uncorrected. The analyses were carried out at Micro-Tech Laboratories, Skokie, Ill. The ultraviolet absorption spectra were measured in aqueous solution on a Beckman DU spectrophotometer.

The Reaction of Nitric Oxide with Dialkyl Phosphonates

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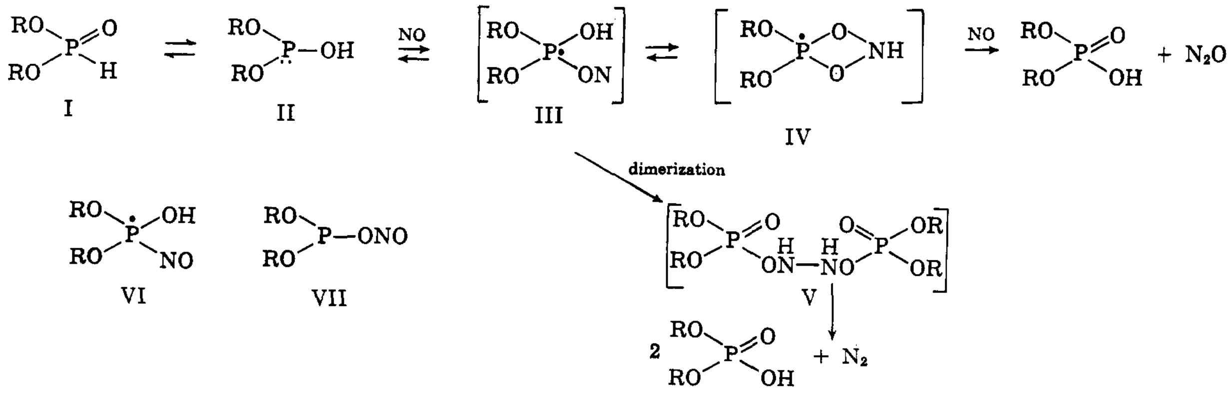
Nitric oxide reacts with dialkyl phosphonates to give the corresponding dialkyl phosphates in high yield. Both tracer experiments with oxygen-18 and the gaseous reaction products indicate that the reaction proceeds *via* two mechanisms.

A number of reactions between derivatives of trivalent phosphorus and various oxides of nitrogen and related compounds have been reported and recently been reviewed.[1]

It appears that nitric oxide is a particularly efficacious reagent for the oxidation of triphenylphosphine[2] and methylphosphines[3] to the phosphine oxides and of triethyl phosphite to triethyl phosphate.[4] In connection with our studies on the properties of the P–H bond,[5] we have examined the reaction of nitric oxide with dialkyl phosphonates and found that the corresponding dialkyl phosphates are formed readily in excellent yield. The reaction occurs at room temperature both with and without a solvent. The gaseous product obtained is mainly nitrogen with some nitrous oxide. The proportion of the latter component is increased on increasing dilution of the phosphonate in benzene solution. In order to elucidate the mechanism, reaction was run using nitric oxide with $\sim$78 atom % O^{18} and diethyl phosphonate. Both the recovered unchanged nitric oxide, and the product nitrous oxide had a considerably reduced O^{18} content (of the order of 57%) indicating that at some stage the oxygen of nitric oxide is in a reversible equilibrium with a normal oxygen atom which in this case can only be the "phosphoryl" oxygen atom of the phosphonate. The following mechanism is proposed on the basis of the products and in order to account for these isotopic results. The isomerization I $\rightleftarrows$ II is well known[6] and, although no physical evidence for the existence of appreciable concentrations of II has been obtained, many reactions of dialkyl phosphonates are assumed to proceed *via* this intermediate.[5] The intermediate III was not isolated but has a radical type structure formed by attack of oxygen on phosphorus and is analogous to one of the structures proposed by Kuhn[4] for the reaction of nitric oxide with triethyl phosphite. His alternative suggestion of compound with a P–N bond (VI) is not likly in this case since the reversible steps II $\rightleftarrows$ III $\rightleftarrows$ IV are required in order to account for the equilibration of isotopic oxygen in the products. In a control experiment nitric oxide was found not to exchange oxygen with diethyl phosphate. The exact structure of IV is not known, but the alternative reaction involving abstraction of hydrogen and attack on *oxygen* by nitric oxide to form compound VII is excluded by the observation that the intermediate in this case, prepared directly from the phosphorochloridite and silver nitrite is known[7] to form tetralkyl pyrophosphate in high



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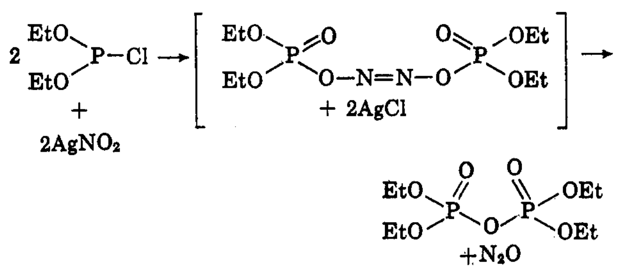
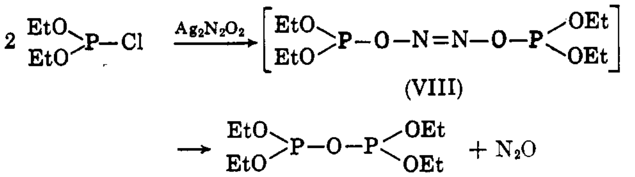
yield. The mechanism of reaction of IV to give products, nitrous oxide and dialkyl phosphate, is not yet understood, but may involve a "nitroxyl" intermediate. It should be noted, however, that recently Hudson[8] has shown that the analogous cyclic carbonyl intermediate was not formed in the reaction of carbonyl chloride with alkyl phosphinates.

Dimerization of the suggested intermediate III to structure V is a type of mechanism that has been proposed in the reaction of nitrosyl chloride and dialkyl phosphonates to form tetraalkyl pyrophosphates.[9] Support for dimers of type V in also provided by the reaction of silver nitrite and diethyl phosphorochloridite to give tetraethyl pyrophosphates and nitrous oxide,[7] the nitrogen–nitrogen bond probably being formed by dimerization of the initial reaction product. A dimer



analogous to V is almost certainly an intermediate[10] (VIII) in the reaction of silver hyponitrite and diethyl phosphorochloridite, breaking down immediately to give tetraethyl pyrophosphite and nitrous oxide.



However, the nitrogen-bridged intermediate (V) suggested for this reaction discussed in this paper differs from the others in that it contains a hydrazo rather than an azo bridge (*cf.* VIII). This may account for the formation of nitrogen rather than nitrous oxide as the second product.

The fact that dialkyl phosphonates react with nitric oxide to give phosphates and with nitrosyl chloride to give pyrophosphates[8,9] indicates that the latter reaction does not involve prior dissociation of nitrosyl chloride to nitric oxide and chlorine. The existence of two competing reactions III to IV and V also is supported by the observation that the proportion of nitrogen in the product is reduced on dilution of the phosphonate component, due to the decreasing chances of dimerization as the concentration of III decreases (*cf.* Table I).

Experimental

Dialkyl phosphonates were prepared from phosphorus trichloride and the corresponding alcohol[11] and twice distilled: dimethyl phosphonate, b.p. 57–58° (9 mm.) [lit.[12] 56–58° (10 mm.)]; and diethyl phosphonate, b.p. 72° (9 mm.) [lit.[13] 72–73 (9 mm.)].

Diethyl phosphate (Hopkins and Williams) was distilled twice, b.p. 118–120° (0.01 mm.) [lit.[14] 116–118° (0.01 mm.)].

Nitric oxide-O^{18} was prepared by equilibration of normal nitric oxide with acidified H_2O^{18}.[15] Both gas and isotopic analyses were carried out on a Consolidated Engineering Corp. 21-405 mass spectrometer.

Action of Nitric Oxide on Dialkyl Phosphonates.—Nitric oxide (Matheson) was bubbled slowly through 10.04 g. of diethyl phosphonate; heat was evolved; and the solution became green. After 3 hr. no further increase in weight occurred; the final weight of the product was 11.08 g. corresponding to an uptake of ~0.99 mole of oxygen per mole of phosphonate. The product was degassed and distilled under high vacuum. A 9.8-g. sample of diethyl phosphate was collected, b.p. 118–119° (0.01 mm.), yield 90%. The product was identified by (a) titration with sodium hydroxide solution, titration equivalent, 159.7, calcd. for $(EtO)_2PO{\cdot}OH$, 154; (b) phosphorus analysis: P found, 19.9%, calcd. for $(EtO)_2PO{\cdot}OH$, 20.1%; (c) the infrared spectra gave peaks at 1230 cm.$^{-1}$ (P=O) and 1040 cm.$^{-1}$ (P—O—Et). No peaks at 945–985 cm.$^{-1}$ (P—O—P) or 2460 cm.$^{-1}$ (P—H) were observed. Similarly dimethyl phosphonate gave dimethyl phosphate in 85% yield, b.p. 105° (0.01 mm.); P found, 25.0%, calcd. for $(MeO)_2PO{\cdot}OH$, 24.6%. To determine the composition of the gaseous products of the reaction, samples of diethyl phosphonate, some in solvent benzene, were sealed in glass ampoules containing nitric oxide. After 7 days at room temperature, the gases were analysed in the mass spectrometer. The results are shown in Table I.

TABLE I

Reaction mixture			Gaseous products, %		
Nitric oxide	Diethyl phosphonate	Solvent	N_2	NO	N_2O
0.22 mmole	...[a]	...	3.2	93.6	3.1
0.22 mmole	0.35 mmole	...	6.4	82.1	11.5
0.22 mmole	0.35 mmole	...	6.5	81.8	11.7
0.22 mmole	0.35 mmole	...	6.5	81.9	11.6
0.55 mmole	0.35 mmole	Benzene	30.2	55.1	14.7
0.55 mmole	0.7 mmole	10 ml.	51.9	28.6	19.5
0.55 mmole	...[a]	Benzene 10 ml.	3.4	93.4	3.1

[a] Blank runs indicate purity of nitric oxide used in these reactions.

Oxygen-18 Tracer Experiments.—Di-*n*-propyl phosphonate (100 mg.) and NO^{18} (~5 ml. at NTP, 77.6 atom % O^{18}) were sealed in glass ampoules and left at room temperature for 7 days. The gases were analyzed mass spectrometrically. Diethyl phosphate was treated similarly. The results are given in Table II.

TABLE II

		Recovered gases, atom % O^{18}	
NO^{18}	Phosphorus ester	NO	N_2O
0.22 mmole	Diethyl phosphonate, 0.7 mmole	55.3	58.5
0.22 mmole	...	77.6	..
0.22 mmole	Diethyl phosphate, 0.7 mmole	74.7	..

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