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# 675. The Mechanism of the Reaction of Nitrosyl Chloride with Dialkyl Phosphonates (The Michalski–Zwierzak Reaction).

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The reaction of nitrosyl chloride with dialkyl phosphonates in several solvents follows second-order kinetics, as measured by the disappearance of nitrosyl chloride. The rate is relatively insensitive to large changes in the dielectric constant of the solvent. No significant kinetic isotope effect is observed on replacing hydrogen bonded to phosphorus by deuterium. The reaction rate is in the order dimethyl > diethyl > di-n-propyl phosphonate. Tracer studies with oxygen-18 show that the oxygen of the product nitrous oxide and of the bridge (P-O-P) oxygen of the tetra-alkyl pyrophosphate are those originally in the nitrosyl chloride. A reaction scheme is suggested involving the formation of the dimer (RO)<sub>2</sub>PO·O·N:N·O·PO(OR)<sub>2</sub>. Support for this structure is provided by the reaction of silver hyponitrite with diethyl phosphorochloridite to give tetraethyl pyrophosphite and nitrous oxide.

An increasing number of reactions have recently been reported between esters of phosphorous acid or phosphines, and oxides of nitrogen and related compounds; they include the oxidation of trialkyl phosphites to phosphates by nitric oxide,<sup>1</sup> and nitrogen dioxide,<sup>2</sup>

<sup>&</sup>lt;sup>1</sup> Kuhn, Doati, and Wellman, J. Amer. Chem. Soc., 1960, 82, 4792.

<sup>&</sup>lt;sup>2</sup> Cox and Westheimer, J. Amer. Chem. Soc., 1958, 80, 5441.

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and of phosphines to phosphine oxides, with nitric oxide,3 nitrogen dioxide,4 or amin oxides.<sup>5</sup> These reactions, many of preparative value, occur with tervalent phosphorus. However, Michalski and Zwierzak have reported<sup>6</sup> an interesting reaction between secondary phosphonates (" phosphites ") and nitrosyl chloride in which tetrasubstituted pyrophosphates are formed.

### $2(RO)_2PO + + 2NOCI \longrightarrow (RO)_2PO + O+PO(OR)_2 + 2HCI + N_2O$

In view of our interest in the properties of the P-H bond <sup>7</sup> and in the synthesis and properties of condensed phosphorus esters,<sup>8</sup> we have examined the mechanism of this reaction by kinetic and isotopic methods.

### Experimental

Materials .-- Dialkyl phosphonates were prepared from phosphorus trichloride and the appropriate alcohol <sup>9</sup> and distilled twice before use: dimethyl, b. p. 57-58°/9 mm. (lit.,<sup>10</sup> b. p. 56-58°/10 mm.); diethyl, b. p. 72°/9 mm. (lit.,<sup>11</sup> 72-73°/9 mm.); di-n-propyl, b. p. 93°/9 mm. (lit.,<sup>12</sup> 91°/9—10 mm.).

Diethyl [phosphoryl-18O]-phosphonate was made by dropping 18O-enriched water (1.32 g., 55 mmoles 82.1% <sup>18</sup>O) (Weizmann Institute) in dioxan (10 ml.) into a stirred solution of diethyl phosphorochloridite <sup>13</sup> (8·1 mmoles) in dry dioxan (20 ml.). Evaporation of the solvent and double distillation of the residue gave diethyl phosphonate (5.5 g., 77%) containing 74.8 atom %excess of oxygen-18 in the phosphoryl group, b. p. 72-73°/9 mm. (lit.,<sup>11</sup> for unlabelled compound, 72-73°/9 mm.).

Di-p-bromobenzyl [phosphoryl-18O]phosphonate was made by the method of Miyano and Funahashi 14 using 18O-enriched water (82.1% 18O) instead of normal water. The product, crystallised twice from benzene-light petroleum, had m. p. 92-93° (lit.,14 93-94°) and contained 62.3 atom % excess of oxygen-18 in the phosphoryl group.

Diethyl [2H]phosphonate was made from phosphorus trichloride and [2H]ethanol as described previously 7c and contained < 2% of the normal compound as estimated from its nuclear magnetic resonance spectra.

Nitrosyl chloride was prepared from sodium nitrite and concentrated hydrochloric acid as described by Morton and Wilcox,<sup>13</sup> and stored as a stock solution (ca. 8%) in benzene.

Diethyl phosphorochloridite (Aldrich Chemical Co.) was distilled twice before use; it had b. p. 65°/28 mm.

Silver hyponitrite was prepared via the reduction of sodium nitrite with sodium amalgam.<sup>15</sup> Solvents were fractionated through a 30 cm. Vigreux column, middle fractions being collected and kept over Linde Molecular Seive 4A (acetonitrile, dioxan, di-n-butyl ether) or sodium wire (benzene, cyclohexane).

Kinetics.—Spectrophotometric method. Michalski and Zwierzak <sup>6</sup> examined the reaction in the presence and absence of pyridine. The present kinetic study was carried out in the absence of pyridine which forms an insoluble hydrochloride during the reaction thus preventing optical density measurements. Also, pyridine is known to form complexes with nitrosyl chloride which would complicate the mechanistic scheme.

Nitrosyl chloride absorbs strongly from approximately  $400-500 \mu$ . The reaction between nitrosyl chloride and three dialkyl phosphonates was followed in a number of solvents by observing the decrease with time of the optical density of the reaction solution at 450  $\mu$ . The

- <sup>3</sup> Abraham, Garland, Hill, and Larkworthy, Chem. and Ind., 1962, 1615.
- <sup>4</sup> Horner and Jurgeleit, Annalen, 1955, 591, 138.
- <sup>5</sup> Howard and Olszewski, J. Amer. Chem. Soc., 1959, 81, 1483.
- <sup>6</sup> Michalski and Zwierzak, Roczniki Chem., 1961, 35, 619; Chem. and Ind., 1960, 376.
- <sup>7</sup> (a) Luz and Silver, J. Amer. Chem. Soc., 1961, 83, 4518; (b) Luz and Silver, J. Amer. Chem. Soc., 1962, 84, 1095; (c) Silver and Luz, J. Amer. Chem. Soc., 1962, 84, 1091.
   <sup>8</sup> Samuel and Silver, Chem. and Ind., 1961, 556; Samuel and Silver, J. Org. Chem., 1963, 28, 1155.
  - <sup>9</sup> McCombie, Saunders, and Stacie, J., 1945, 380.
  - Milobendszki and Sachnowsky, Chem. Polsk., 1917, 15, 34.
     Strecker and Spitaler, Ber., 1926, 59, 1754.

  - <sup>12</sup> Arbuzov, Ber., 1905, **38**, 1171.

  - <sup>13</sup> Morton and Wilcox, *Inorg. Synth.*, 1953, 4, 48.
     <sup>14</sup> Miyano and Funahashi, *J. Amer. Chem. Soc.*, 1955, 77, 3522.
  - <sup>15</sup> Brauer, "Handbuch der Präparativen Anorganischen Chemie," F. Enke, Stuttgart, 1960, p. 442.

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optical density of solutions of nitrosyl chloride was found to be a linear function of concentration up to at least 70 µmoles per ml., in all the solvents used. The optical density at 450 mµ of a nitrosyl chloride solution of given concentration varied between different solvents, hence the calibration curves were determined for each solvent separately. The stock solution was standardised by the total hydrolysis of a measured volume with a slight excess of sodium hydroxide solution and gravimetric determination of chloride ion as silver chloride.<sup>16</sup> In a typical run a sample of phosphonate (5–20 mg.) was weighed out in a Beckmann 1 cm. glass cell fitted with a ground glass stopper; solvent (2·7 ml.) was carefully run into the cell leaving the phosphonate largely undissolved at the bottom of the cell; a carefully measured volume of nitrosyl chloride stock solution was run into the cell from a micropipette; the cell was stoppered, shaken, and a stop-watch started. Readings of optical density were made at 450 µ against a blank cell containing only solvent. All runs were followed to over 95% reaction. The kinetic data were analysed in terms of a bimolecular second-order reaction between nitrosyl chloride and phosphonate. Second-order rate constants were obtained graphically from a plot of log[(a - x)/(b - x)] against time, and are tabulated in Tables 1 and 2.

### TABLE 1.

Second-order rate constants (at  $23^{\circ} \pm 0.2^{\circ}$ ) for the reaction between nitrosyl chloride and dialkyl phosphonates.

102[NOC]]	$10^{2}$ (FtO), PO·H1		k (mole	10 <sup>2</sup> [NOCI1_1	$10^{2}$ (FtO) PO·F	-TI	k (mole
(moles $l^{-1}$ )	(moles $1.^{-1}$ )	Solvent	$1.^{-1}$ min.)	(moles $1, -1$ )	$(moles 1.^{-1})$	Solvent	$l_{1}^{-1}$ min.)
4.08	5.69	Benzene	5.10	4.08	2.61	Diovan	4.92
4.08	2.82	Denzene	5.22	4.08	0.036	DIOXall	4.01
5.71	2.95	,,	5.00	4.08	1.09	,,	9.09
0.71	2.00	,,	5.09	4.00	1.09	,,	3.98
2.85	2.87	,,	5.15	2.04	2.89	**	4·12
1.63	2.87	,,	5.45	6.15	2.89	,,	$4 \cdot 20$
0.612	2.79	,,	5.18	4.08	2.82	Cyclo-	10.9
0.273	2.85	,,	4.98			hexane	
<b>4</b> ·89	2.82	,,	5.10	6.12	2.79	,,	10.4
4.08	4.44		5.40	11.0	2.82		10.8
<b>4</b> ·08	1.48		5.31				
4.08	2.79	Dibutyl	14.7	$10^{2}[(MeO)_{2}PO\cdot H]$			
- • •		ether		4.08	3.57	Benzene	8.74
4.08	2.72		15.4	2.04	3.57		8.82
2.04	2.77	,,	15.0	4.08	1.77		9.06
6.12	2.82	,,	15.5			••	
4.00	1.49	,,	15.4	$10^{2}[(Pr^{n}O), PO \cdot H]$			
4.00	1.42	,,	10.4	4.08	6.97	Bonzono	2.11
4.08	0.754	,,	14.8	4.00	0.21	Déuveue	0.00
				4.08	4.42	,,	3.20
				6.15	2.27	••	<b>3</b> ·00

### TABLE 2.

# Deuterium isotope effects on the reaction between nitrosyl chloride and diethyl phosphonate.

	1	$k_2$ (mole l. <sup>-1</sup> min.)		$k_2$
Diethyl phosphonate Diethyl [ <sup>2</sup> H]phosphonate	In cyclohexane	{10·7 (3 runs) 10·8 (3 runs)	In di-n-butyl ether	$ \begin{cases} 15.1 & (6 \text{ runs}) \\ 14.8 & (3 \text{ runs}) \end{cases} $

Gasometric method. A solution of diethyl phosphonate (57 mmoles) and nitrosyl chloride (57 mmoles) in cyclohexane (135 ml.) was placed in a thermostated flask with a magnetic stirrer and connected to a manometer. The evolved gases were passed over potassium hydroxide pellets to remove hydrogen chloride. The manometer was read at 30 sec. intervals. The cyclohexane was previously saturated with nitrogen to reduce the solubility of nitrous oxide in the solvent.

Tracer Experiments.—Nitrous oxide. The origin of the oxygen atom in the nitrous oxide produced in the reaction was determined as follows. Diethyl [phosphoryl-18O]phosphonate (0.26 ml.) was dissolved in dry benzene (1.2 ml.) in one arm of a Rittenberg tube. Nitrosyl chloride in benzene (ca. 8%; 1.5 ml.) was introduced into the other arm. The tube was closed, placed in liquid air to freeze the solutions, and evacuated (~ 10 microns). After warming to room temperature, the solutions were mixed by tilting the tube. After the reaction was

<sup>16</sup> Kolthoff and Sandell, "Textbook of Quantitative Inorganic Chemistry," Macmillan, New York, **1948**, p. **307**.

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complete, as shown by disappearance of the colour of nitrosyl chloride, the reaction vessel was cooled in an ice-bath and samples of the gaseous products removed for mass spectrometric analysis by transfer on the vacuum line to sealed tubes provided with break-off tips. In some cases the ampoules contained a pellet of potassium hydroxide to remove possible contaminating acidic products such as carbon dioxide or nitrogen dioxide.

The whole procedure was also repeated with the addition of pyridine (0.17 ml.) to the reaction solution in order to trap hydrogen chloride. The diethyl phosphonate contained 74.8 excess atom % of oxygen-18 in the phosphoryl group, and the nitrous oxide product contained 3.27 and 2.12 excess atom % of oxygen-18 in the first and the second case, respectively; in the second the gas was collected over potassium hydroxide.

In the tetrasubstituted pyrophosphate formed by the reaction of nitrosyl chloride with dialkyl [18O]phosphonate, the oxygen-18 can be in the phosphoryl position, in the bridge oxygen, or distributed between the two. Dudek and Westheimer <sup>17</sup> have shown that tetrabenzyl pyrophosphate reacts with proposide ion in propanol with 100% P-O bond fission to give dibenzyl pyrophosphate and dibenzyl propyl phosphate.

$$[(PhCH_2 \cdot O)_2 PO]_2 O + PrO^{-} \longrightarrow (PhCH_2 \cdot O)_2 PO \cdot OPr + (PhCH_2 \cdot O)_2 PO_2^{--}$$

When this reaction is applied to the two extremes of <sup>18</sup>O-labelling in the product of our tracer experiments, the consequences are as shown in reactions (1)—(3).

$$\begin{array}{cccc} {}^{18} O & {}^{18} O & {}^{18} O \\ (RO)_2 P \times {}^{18} & P (OR)_2 & \longrightarrow & (RO)_2 P - OPr & + & {}^{-}O - P (OR)_2 \end{array}$$

$$\begin{array}{cccc} (RO)_2 P & - OPr & + & {}^{-}O - P (OR)_2 \end{array}$$

$$\begin{array}{cccc} (2) &$$

$$(RO)_{2}P_{18} \xrightarrow{P(OR)_{2}} (RO)_{2}P_{-OPr} + \xrightarrow{I8}_{O} (P(OR)_{2} (3)$$

Reaction (1) can be written only one way since the tracer is distributed symmetrically. Reactions (2) and (3) represent two possible distributions of tracer in the reaction products, because propoxide ion may attack at either of the two non-equivalent (with respect to oxygen-18) phosphorus atoms. On the assumption that reactions (2) and (3) are equally probable, the result would be that the diester would contain three atoms of oxygen-18 in eight oxygen atoms while the triester would contain one atom of oxygen-18 in eight oxygen atoms. Reaction (1) would give a diester and a triester each with one atom of oxygen-18 in four oxygen atoms.

In order to facilitate the purification of the products for isotopic analysis, and to avoid possible rearrangements caused by the high-temperature distillation needed to separate liquid alkyl phosphonates and pyrophosphates, the tracer studies were carried out using di-p-bromobenzyl phosphonate. This compound gives a crystalline pyrophosphate, which on reaction with propoxide ion gives crystalline di- and tri-substituted phosphates.

Di-p-bromobenzyl [<sup>18</sup>O]phosphonate (2·1 g.) and pyridine (0·42 g.) were dissolved in benzene (15 ml.), and nitrosyl chloride (ca. 8%) in benzene (6 ml.) was added slowly with stirring. After 30 min. at room temperature, the pyridine hydrochloride was filtered off and the filtrate evaporated *in vacuo* at room temperature. The resulting residue was recrystallised twice from ethanol to give tetra-p-bromobenzyl pyrophosphate (0·58 g.), m. p. 103—104° (lit., <sup>6</sup> 105—105·5°). The pyrophosphate was dissolved in dry propanol (40 ml.) and sodium propoxide in propanol (0·54N; 2·5 ml.) added. After 90 min. at room temperature, the solvent was removed *in vacuo* 

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<sup>&</sup>lt;sup>17</sup> Dudek and Westheimer, J. Amer. Chem. Soc., 1959, 81, 2641.

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at room temperature and the residue shaken with a mixture of benzene and saturated sodium hydrogen carbonate solution. The benzene layer was washed several times with sodium hydrogen carbonate solution and water, dried  $(Na_2SO_4)$ , heated with decolorising carbon, filtered, and evaporated to give a white crystalline residue. Recrystallisation to constant m. p. from light petroleum-pentane gave di-p-bromobenzyl propyl phosphate, m. p. 41-42°, no depression on mixing with synthetic di-p-bromobenzyl propyl phosphate prepared as described below. The combined sodium hydrogen carbonate and water layers were acidified (HCl) to give a white flocculent precipitate which was extracted into chloroform. The chloroform solution was dried (Na<sub>2</sub>SO<sub>4</sub>), warmed with decolorising carbon, filtered, and evaporated to give di-p-bromobenzyl phosphate, m. p. 158° (from ethanol-water) (lit., 18 157-158°). The whole procedure described above was also carried out in the absence of pyridine.

The products of propanolysis were analysed for oxygen-18.

Di-p-bromobenzyl phosphate (A) (excess atom % of <sup>18</sup> O)	15·2 ª	15·4 ª	16·4 <sup>b</sup>
Di-p-bromobenzyl propyl phosphate (B) (excess atom % of <sup>18</sup> O)	12.9	14.4	17.2
Ratio (A)/(B)	1.18	1.07	0.95

<sup>a</sup> Pyridine present. <sup>b</sup> Pyridine absent.

Di-p-bromobenzyl propyl phosphate, one of the products of the reaction between proposide and tetra-p-bromobenzyl pyrophosphate, has not been previously described. In order to check the identity of this product it was synthesised by an alternative method. Sulphuryl chloride (0.4 ml., ca. 5 mM) was added to di-p-bromobenzyl phosphonate (5 mM) suspended in carbon tetrachloride (25 ml.). After 20 min. the solvent and evolved gases were removed under reduced pressure at room temperature and the crude di-p-bromobenzyl phosphorochloridate dissolved in benzene (25 ml.) and added to a solution of propanol (2 ml.) and pyridine (3 ml.) in dry benzene (15 ml.). After 3 hr. at room temperature the solution was washed with dilute hydrochloric acid, water, and aqueous sodium hydrogen carbonate solution. The benzene solution was dried  $(Na_2SO_4)$ , warmed with decolorising carbon, filtered, and evaporated. The residue was crystallised from light petroleum-pentane to constant m. p. 42°, undepressed on admixture with the triester obtained from the propanolysis of tetra-p-bromobenzyl pyrophosphate (Found: C, 44·1; H, 4·87; P, 6·02. Calc. for C<sub>17</sub>H<sub>19</sub>Br<sub>2</sub>O<sub>4</sub>P: C, 42·6; H, 3·98; P, 6.49%). The yield based on di-*p*-bromobenzyl phosphonate was 17%.

Isotopic Analyses.—Nitrous oxide was analysed for oxygen-18 by scanning masses 44—46 in a Consolidated Engineering Corp. mass spectrometer MS 21-401. All other compounds were converted into carbon dioxide by the method of Anbar and Guttmann<sup>19</sup> and analysed for oxygen-18 by scanning masses 44-48.

Reaction of diethyl phosphorochloridite and silver hyponitrite. Diethyl phosphorochloridite (1.56 g.) in benzene (5 ml.) was added slowly to silver hyponitrite (1.38 g.) in dry benzene (10 ml.) in a flask protected from moisture by a calcium chloride tube. After a brief induction period an exothermic reaction occurred accompanied by the evolution of gas. The resulting dark brown solution was distilled to give tetraethyl pyrophosphite (0.6 g.), b. p.  $68^{\circ}/0.01 \text{ mm}$ . (lit.,<sup>20</sup>  $82-83^{\circ}/2-3$  mm.). The product was identified by determination of the oxidation equivalent with iodine (Found: 127. Calc. for  $C_8H_{20}O_5P_2$ : 129), by oxidation <sup>8</sup> with nitrogen dioxide to give a product having infrared spectrum identical with that of tetraethyl pyrophosphate, and by phosphorus analysis (Found: P, 23.8. Calc. for  $C_8H_{20}O_5P_2$ : P, 24.0%). The gaseous products were collected by the procedure used in the reaction of nitrosyl chloride with phosphonates. Mass-spectroscopic analysis showed the presence of nitrous oxide (78%) and nitrogen (19%).

### DISCUSSION

On the basis of the kinetic and isotopic results, the following scheme is suggested; it is an extension of one of the alternatives suggested by Michalski and Zwierzak.<sup>6</sup> Step (1) is a second-order reaction analogous to the formation of phosphorochloridates from chlorine and phosphonates. The excellent second-order plots obtained indicate

 <sup>&</sup>lt;sup>18</sup> Baddiley, Clark, Michalski, and Todd, J., 1949, 815.
 <sup>19</sup> Anbar and Guttmann, Internat. J. Appl. Radiation Isotopes, 1959, 3, 233.

<sup>&</sup>lt;sup>20</sup> Arbuzov and Arbuzov, Zhur. obshchei Khim., 1932, 2, 348.

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that the hydrogen chloride produced does not catalyse the reaction at the concentrations studied. As in the case of hydrogen-exchange,7 oxidation,21 and hydrolysis,22 the order

$$2(RO)_{2}PO \cdot H + 2NOCI \xrightarrow{I} [(RO)_{2}PO \cdot NO] \text{ or } [(RO)_{2}PO \cdot ON]$$

$$(I) \qquad \qquad (II)$$

$$V_{2}O + (RO)_{2}PO \cdot O \cdot PO(OR)_{2} \xleftarrow{I} [(RO)_{2}PO \cdot O \cdot N \cdot N \cdot O \cdot PO(OR)_{2}]$$

$$(III)$$

of reaction is dimethyl > diethyl > di-n-propyl. This order suggests that nitrosyl chloride is acting as a nucleophilic reagent.

The rate-determining step in the oxidation of dialkyl phosphonates by halogens in aqueous solution is the formation of a tercovalent "phosphite" form: 7 (RO),PO·H (RO), P·OH. This tautomeric shift is very slow in the non-hydroxylic solvents used in the present study,23 the rate being several orders of magnitude slower than typical rates for reaction with nitrosyl chloride. Thus the reaction with nitrosyl chloride is not preceded by a tautomeric shift.

Replacement of the phosphorus-bonded hydrogen by deuterium has no significant effect on the rate in cyclohexane and in dibutyl ether (Table 2), for reasons which are not clear. A small isotope effect was observed in the acetate-catalysed oxidation of diethyl phosphonate  $(k_{\rm H}/k_{\rm D} = 1.07)$  and explained in terms of a three-centre transition state.<sup>7</sup> The breaking of the P-H bond may here be a fast step subsequent to the rate-determining formation of a quinquecovalent intermediate. Further work on isotope effect on the P-H bond is needed before a more definite interpretation can be offered. The comparative insensitivity of the rate to large changes in solvent dielectric constant (Table 1) indicates that only small differences occur in charge separation between the reactant and the transition state. A four-centre transition state may possibly be involved. P-nitrosocompounds of types (I) and (II) have not yet been isolated although Kuhn<sup>1</sup> has suggested that the intermediate (RO)<sub>3</sub>R·ON occurs in the reaction between nitric oxide and trialkyl phosphites, and intermediate (II) almost certainly occurs in the reaction of silver nitrite with diethyl phosphorochloridite to give tetraethyl pyrophosphate.<sup>24</sup> Michalski's failure to isolate compounds of type (I) is probably a consequence of the known tendency of nitroso-compounds to dimerise.<sup>25</sup> Whilst there is no direct evidence for (I) or (II), the oxygen-18 tracer results from the present work show that the original phosphoryl oxygen of the phosphonate remains undisturbed throughout the reaction, the bridge oxygen of the pyrophosphate coming entirely from the nitrosyl chloride.

We suggest that the dimeric structure (III) is the immediate precursor of tetra-alkyl pyrophosphates. An attempt to prepare intermediate (III) directly by the reaction of diethyl phosphorochloridate and silver hyponitrite failed owing to the stability of the P-Cl bond under the various reaction conditions tried. However, diethyl phosphorochloridite reacted readily at room temperature to give tetraethyl pyrophosphite and nitrous oxide and almost certainly proceeds via a bridged azo-structure (IV). Compound

> $2(EtO)_2PCI + Ag_2N_2O_2 \longrightarrow [(EtO)_2PONNNOP(OEt)_2] + 2AgCI$ ↓ (IV)  $(EtO)_2 P \cdot O \cdot P(OEt)_2 + N_2 O$

(IV) is the phosphorous analogue of (III; R = Et). The dimension step of (II) to give

- <sup>23</sup> Reuben and Silver, unpublished results.
  <sup>24</sup> Samuel and Silver, *Chem. and Ind.*, 1962, 2063.
- <sup>25</sup> Gowenlock, Quart. Rev., 1958, 12, 321.

<sup>&</sup>lt;sup>21</sup> Nylen, Z. anorg. Chem., 1938, 235, 161.

<sup>&</sup>lt;sup>22</sup> Nylen, Svensk. kem. Tidskr., 1937, 49, 29.

(III) is strongly supported by the reaction of silver nitrite with diethyl phosphorochloridite to give tetraethyl pyrophosphate and nitrous oxide.<sup>24</sup> The reaction may be formulated

This reaction demonstrates that an intermediate with the stoicheiometry of (II) can dimerise and subsequently rearrange to give tetra-alkyl pyrophosphate.

It is of interest to note that an analogous structure to (III) has been isolated from the reaction of oxalyl chloride and dibenzyl phosphate,<sup>26</sup> which on heating breaks down to give tetrabenzyl pyrophosphate, carbon monoxide, and carbon dioxide.

 $2(PhCH_{2} \cdot O)PO \cdot OH + (COCI)_{2} \longrightarrow (PhCH_{2} \cdot O)_{2}PO \cdot O \cdot CO \cdot CO \cdot O \cdot PO(O \cdot CH_{2}Ph)_{2}$ 

Abraham et al.<sup>3</sup> have recently suggested that the oxidation by nitric oxide of Group V organometallic compounds proceeds via the following mechanism. Structures (V) and (VI) are similar to (II) and (III), respectively; particularly relevant is the suggestion of the initial formation of the nitrogen-nitrogen bond, in complete analogy to the dimerisation of (II) to give (III) as suggested in the present work. Nevertheless structure (III) can be



formed by rearrangement of the dimer (VII) based on structure (I). Both mechanisms for the formation of (III) keep the phosphoryl oxygen intact, which is consistent with the oxygen-18 tracer results. Compounds with similar structure to (VII) are known to rearrange in order to increase the number of bonds to oxygen.

Other cyclic rearrangements of oxygen to phosphorus are found in the thermal decomposition 27 of N-benzoylphosphorimidic trichloride and in the many reactions of the "Wittig" 28 type. Similarly, Bunyan and Cadogan 29 have suggested the following reaction scheme in the nitrosation of phosphoramides. This is based on analogy with rearrangements in carbon chemistry of N-nitrosoacylarylamines<sup>30</sup> (VIII; R = Me, R' = Ph) and of N-nitrosoamides of secondary carbinamines <sup>31</sup> (VIII; R = cyclohexyl or phenylethyl, R' = naphthyl) and of esters of N-acetyl-N-nitrosoglycine<sup>32</sup> (IX). The mechanism of rearrangements of three 27,31,32 of these reactions has also been elucidated using oxygen-18. If the dimerisation and the subsequent collapse of the dimer are very fast compared with the initial reaction with nitrosyl chloride it follows that the observed rates of disappearance of the latter and appearance of nitrous oxide should be equal. An

- <sup>26</sup> Mason and Todd, J., 1951, 2267.
   <sup>27</sup> Lapidot and Samuel, J., 1962, 2110.
   <sup>28</sup> Schöllkopf, Angew. Chem., 1951, **71**, 260.

- <sup>29</sup> Schöhkopf, Angew. Chem., 1894, 14, 200.
   <sup>29</sup> Bunyan and Cadogan, J., 1962, 1304.
   <sup>30</sup> Hey, Stuart-Webb, and Williams, J., 1952, 4657.
   <sup>31</sup> White and Aufdermarsh, J. Amer. Chem. Soc., 1958, 80, 2597.
   <sup>32</sup> Reimlinger and Skatteböl, Chem. Ber., 1961, 94, 2429.

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attempt was made to follow the kinetics of nitrous oxide evolution by a manometric method. The results were analysed on the basis of the suggested reaction scheme, assuming that steps (1) and (2) are much slower than the subsequent (presumably intramolecular) steps. In this case the overall reaction may be treated as the sum of two



consecutive bimolecular reactions, steps (1) and (2). Chien<sup>33</sup> has given expressions for the rate of product formation in such a case. When the results of the manometric experiments are plotted according to his method, the experimental points fall close to a line plotted for  $k = k_2/k_1 = 50$ , indicating that  $k_2$  for step (2) is approximately fifty times larger than step (1), where  $k_1$  and  $k_2$  are bimolecular rate constants. Such an analysis is, however, based on too many assumptions to carry much weight, but the results suggest that the steps following step (1) are very fast, whatever their nature.

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33 Chien, J. Amer. Chem. Soc., 1948, 70, 2256.