reaction solution was then poured into 150 ml. of ether–100 ml. of water. The ether was washed with water, dried over sodium sulfate and evaporated under reduced pressure. Distillation of the residue gave 3.6 g. (67%) of brominated 1-methyl-6-nitrocyclohexenes, b.p. 60–75° (0.2 mm.). Infrared analysis[22] showed that this material consisted of about 60% of 6-bromo-1-methyl-2-nitrocyclohexene (conjugated nitro absorption at 6.56 μ) and about 40% of 6-bromo-1-methyl-6-nitrocyclohexene (unconjugated nitro absorption at 6.40 μ). The mixture was redistilled for analysis and boiled at 65–71° (0.2 mm.). Infrared analysis of this material gave 59% of conjugated nitro derivative and 41% of unconjugated nitro derivative.

Anal.[25] Calcd. for $C_7H_{10}BrNO_2$: C, 38.20; H, 4.58; N, 6.37. Found: C, 37.97; H, 4.71; N, 6.53.

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[25] The author wishes to thank Mrs. O. Hamerston for the analysis.

Reaction of Polyglycols with Phosphorus Pentafluoride

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Diethylene glycol and polyglycols, as well as their diethers, gave dioxane upon treatment with phosphorus pentafluoride. Under the same conditions, bis-1,4-hydroxyethylpiperazine was synthesized from diethanolamine and thiodiethylene glycol gave both 1,4-oxathiane and 1,4-dithiane.

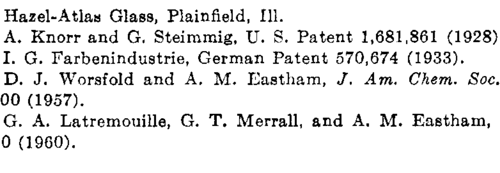
The early patent literature[2] reveals that ethylene and diethylene glycols as well as the monoethyl ether of diethylene glycol can be converted to dioxane by refluxing with catalytic amounts of concentrated sulfuric acid. Later work[3] describes similar results with polyethylene and polypropylene glycols. However, very few experimental data are given in either reference.

Eastham and his co-workers[4] have shown that in the cationic polymerization of ethylene oxide, for example with stannic chloride or boron trifluoride, some depolymerization of polyglycol occurs with concomitant formation of dioxane.

On the other hand it was observed[5] that triethyloxonium fluoroborate (Et_3OBF_4) caused almost complete depolymerization of polyethylene glycols to dioxane. It also has been reported[6] that ethylene and propylene oxides and even tetrahydrofuran can be polymerized by phosphorus pentafluoride to the corresponding polyglycols; however, there is no mention made of any depolymerization of the products.

This report describes the reaction of certain polyglycols and their derivatives with catalytic amounts of phosphorus pentafluoride to yield dioxane under relatively mild conditions.

The reaction can be represented as



Dioxane was formed in the above reaction from the glycols, their diethers, and diesters. However, under the same reaction conditions, the monoethers of ethylene and diethylene glycols did not produce dioxane and the starting materials were recovered in most part unchanged. An explanation of this anomaly is not obvious.

It should also be noted that the by-product of this reaction proved to be water from the glycols themselves and the corresponding ether from the glycol diethers; for example, dimethyl ether was isolated and identified from the dimethyl ether of diethylene glycol. In like manner the diacetate of diethylene glycol gave acetic anhydride as the by-product along with dioxane.

When diethanolamine was treated with phosphorus pentafluoride only trace amounts of morpholine were obtained. Instead, bis-1,4-dihydroxyethylpiperazine was isolated in 30% yield. Thiodiethylene glycol under the same conditions gave mainly 1,4-oxathiane along with lesser amounts of 1,4-dithiane.

Experimental

General Reaction Procedure of Phosphorus Pentafluoride with Substituted Glycols.—In a 500-ml. three-neck flask fitted with a condenser, sealed stirrer, and a Weston dial thermometer, 0.25 to 1.0 mole of glycol and, respectively, 0.025 to 0.1 mole *p*-chlorophenyldiazonium hexafluorophosphate were added. The use of less than 10 mole % of *p*-chlorophenyldiazonium hexafluorophosphate decreased the yield measurably, whereas an excess of 10 mole % did not increase the yield of the reaction. Since *p*-chlorophenyldiazonium hexafluorophosphate decomposed between 100–150° to yield pure phosphorus pentafluoride, the reaction mixture was heated to 120–150° and stirred for 24 hr. The mixture then was distilled twice from a Claisen head and

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[1] Hazel-Atlas Glass, Plainfield, Ill.

[2] A. Knorr and G. Steimmig, U. S. Patent 1,681,861 (1928).

[3] I. G. Farbenindustrie, German Patent 570,674 (1933).

[4] D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 897, 900 (1957).

[5] G. A. Latremouille, G. T. Merrall, and A. M. Eastham, *ibid.*, **82**, 120 (1960).

[6] E. L. Muetterties, U. S. Patent 2,856,370 (1958).

fractionated using an 18-in. Widmer column. The dioxane fraction boiled from 99–101°. The products were analyzed and identified by boiling point, refractive index, gas chromatography, and infrared spectrophotometry. The types of glycols used in this reaction and yields of product are listed in Tables I and II.

TABLE I
REACTIONS OF SUBSTITUTED GLYCOLS WITH PHOSPHORUS PENTAFLUORIDE[a]

Compound	% Yield of cyclic product[b]	Other products identified
Diethylene glycol	86% Dioxane	Water
Polyethylene glycol (400)[c]	80% Dioxane	Water
Polypropylene glycol (2025)[c]	30% Dimethyl dioxanes	Water, polymer, ten unidentified trace products
Diethylene glycol dimethyl ether	88% Dioxane	Dimethyl ether
Diethylene glycol diethyl ether	70% Dioxane	Diethyl ether
Diethylene glycol dibutyl ether	30% Dioxane	Dibutyl ether
Tetraethylene glycol dibutyl ether	10% Dioxane	Dibutyl ether
Diethylene glycol diacetate	78% Dioxane	Acetic anhydride
Thiodiethylene glycol	70% 1,4-Oxathiane 10% 1,4-Dithiane	Water
Diethanolamine	30% 1,4-Dihydroxyethylpiperazine	Water, diethanolamine, traces of morpholine

[a] The reaction conditions were 10 mole % phosphorus pentafluoride catalyst in the form of *p*-chlorophenyldiazonium hexafluorophosphate which decomposes to give off PF_5 at 100–150°. Reaction temperature was 120–150° for approximately 24 hr. [b] The percentage of cyclic product in most cases is an average of several experiments on the same compound as determined by gas chromatography. [c] Numbers in parenthesis refer to molecular weight of the polyglycols.

Generation of Pure Phosphorus Pentafluoride Gas for Reaction with Dimethyl Ether of Diethylene Glycol.—In order to demonstrate that phosphorus pentafluoride was the catalyst which caused the reaction, 29 g. (0.1 mole) of *p*-chlorophenyldiazonium hexafluorophosphate was heated slowly in a dry flask at 90–130°. The gases evolved were passed through two Dry Ice traps and bubbled into 134 g. (1.0 mole) of pure dry dimethyl ether of diethylene glycol which was heated at 70–100°. The entire system was kept anhydrous at all times. The reaction time was 2 hr. and the product was distilled and subsequently fractionated using and 18-in. Widmer column, collecting 31 g. (35%) of dioxane boiling at 99–101°; n^{20}_{D} 1.4220. The low yield in this case probably was due to the short reaction time. The reported constants for dioxane are: b.p. 101.3°, n^{20}_{D} 1.4224.[7]

Reaction of Dimethyl Ether of Diethylene Glycol with Phosphorus Pentafluoride in the Presence of Quinone.—The general reaction procedure was carried out on a molar basis as described above. However, 10.8 g. of quinone was added to the reaction mixture which was heated at 120° for 16 hr. The yield of dioxane was 68 g. (79%), indicating no inhibition of reaction due to the presence of quinone as a free radical scavenger.

TABLE II
ATTEMPTED REACTIONS OF SUBSTITUTED GLYCOL WITH PHOSPHORUS PENTAFLUORIDE[a]

Compound	% Starting material[b] recovered	% Material[c] balance	Remarks
Ethylene glycol monoethyl ether	89	94	Solid residue
Ethylene glycol monobutyl ether	95	91	Solid residue
Ethylene glycol mono-*n*-hexyl ether	91	94	Solid residue
Ethylene glycol dibutyl ether	90	92	Solid residue
Diethylene glycol monomethyl ether	98	94	Solid residue
Diethylene glycol monoethyl ether	90	91	Solid residue
Diethylene glycol ethyl ether monoacetate	76	92	10% Dioxane and ethyl acetate and 10% residue
Dichlorodiethyl ether	85	89	Solid residue
Morpholine	86	91	Some solid residue

[a] The reaction conditions were the same as mentioned in Table I. [b] The starting material recovered was verified in some cases by gas chromatography or by boiling point, refractive index, and infrared analysis. [c] The material balance was obtained from the total starting material and total reaction product in order to demonstrate that phosphorus pentapentafluoride had been liberated but did not react.

Action of Phosphorus Pentafluoride on Thiodiethylene Glycol.—The general reaction procedure was followed with 0.5 mole of thiodiethylene glycol and no starting material was recovered. The product consisted of 37 g. (70%) of 1,4-oxathiane boiling at 146° n^{20}_{D} 1.5082. The reported values for this substance are b.p. 147° and the mercuric chloride derivative of 1,4-oxathiane was prepared as needles from ethanol, m.p. 170°. The reported[8] value is 171°. The residue from the distillation was crystallized and subsequently recrystallized from ethanol. The melting point was 111°. The reported melting point of 1,4-dithiane is 111°.[9]

The mercuric chloride derivative was prepared and recrystallized from alcohol, m.p. 230° with decomposition. The reported value[6] is above 200°.

Effect of Phosphorus Pentafluoride on Diethanolamine.—The general reaction procedure was followed. Upon cooling to room temperature, the reaction mixture solidified. The mixture was dissolved in alcohol and filtered. The alcohol solution was decolorized with activated charcoal. The alcohol was evaporated and the light brown oil was crystallized from hot ethyl acetate. After five recrystallizations from ethyl acetate, needles were obtained melting at 136°. Upon sublimation the purified material melted at 138°. The molecular weight was obtained by the Rast-Camphor method and by a pH titration equivalence. The average molecular weight was 179. The compound was basic and extremely soluble in water and alcohol with negative tests for any halogen.

Anal. Calcd. for $C_8H_{18}N_2O_2$: C, 55.0; H, 10.3, N, 16.05. Found: C, 54.69; H, 9.91: N, 15.65.

The molecular weight and formula correspond to bis-1,4-dihydroxyethylpiperazine. The reported melting point is 134–135°.[10] Maximum yields corresponded to 30%.

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(7) K. Hess and H. Frahm, *Ber.*, **71B**, 2627 (1938).

(8) H. T. Clark, *J. Chem. Soc.*, **101**, 1806 (1912).

(9) A. Husemann, *Ann.*, **126**, 269 (1863).

The picrate melted with decomposition at 245°. The reported m.p. for the picrate of 1,4-bis(β-hydroxyethyl)-piperazine is 245–246°. The dihydrochloride also was prepared, m.p. 204°, the reported value is 200–202°.

Preparation of Diethylene Glycol Acetates.—The diacetate of diethylene glycol and the acetate of the monoethyl ether of diethylene glycol were prepared conventionally by the action of 500 ml. of pure acetic anhydride and 10 ml. of dry pyridine on 0.75 mole of the corresponding glycol. Infrared spectra of the products showed no hydroxyl groups present. The diacetate of diethylene glycol was obtained in 50% yield, boiling at 110° at 7-mm. pressure, n^{20}_{D} 1.4300. The reported value is b.p. 148° at 26-mm. pressure.[11] The acetate of the monoethyl ether of diethylene glycol was obtained in a 40% yield, boiling at 85° at 7-mm. pressure, n^{20}_{D} 1.4210. These also were subjected to the general reaction procedure with the results listed in Tables I and II.

Attempted Reaction of Phosphorus Pentafluoride with Morpholine.—The general reaction procedure was followed as already described. Little or no reaction took place. The recovery of morpholine from the reaction mixture was 86%.

Attempts to Demonstrate a Reversible Reaction.—A charge of 44 g. (0.5 mole) of pure dioxane, 37 g. (0.5 mole) of dry ethyl ether, and 14.5 g. (0.05 mole) of p-chlorophenyldiazonium hexafluorophosphate was placed into a 250-ml. autoclave. The temperature was maintained at 100–110°. The pressure was at 170 p.s.i. for 24 hr. The autoclave was cooled in ice and opened. The mixture was fractionally distilled on an 18-in. Widmer column and 25 g. of ethyl ether and 40.2 g. of dioxane (91.4%) were recovered. The reaction was repeated at 200° with a pressure of 340 p.s.i. for 48 hr. Again, 90% of the dioxane was recovered.

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[10] F. L. Pyman, *J. Chem. Soc.*, **93**, 1802 (1908).

[11] L. H. Cretcher and W. J. Pittenger, *J. Am. Chem. Soc.*, **47**, 163 (1925).

A New Route to N-Arylphosphoramidic Acids[1a]

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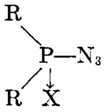
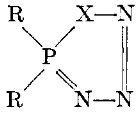
Some representative phosphoryl azides which we have synthesized possess infrared absorptions consistent with acyclic structures. The aminolysis of one such azide, and some related compounds, has been explored. In refluxing aniline, diethyl phosphoryl azide[1c] (IVa) underwent not only P—N bond cleavage but also alkyl-oxygen scission, the product being N-phenylphosphoramidic acid (Va). Compound Va was also formed when either diethyl phosphorochloridate (IVb), or O,O-diethyl N-phenylphosphoramidate (IVc), was used as the aminolysis substrate. These reactions constitute a new route to N-arylphosphoramidic acids. The mechanism of the process is discussed.

We have established elsewhere[2a] that the so-called thiocarbamyl azides are really thiatriazoles and that a similar cyclization is not apparent with the oxy analogs, the carbamyl azides. It was of interest to extend these observations to phosphorus systems and to determine whether substituted phosphoryl azides are open-chain compounds (Ia, Ib) or heterocyclic (IIa, IIb). As in our previous work[2a] our structural assignments were based on infrared data. The first of the azides we prepared, namely IIIa, showed a strong azide stretching absorption at *ca.* 2140 cm.$^{-1}$, corresponding[2b,3] to the acyclic formulation.



Ia. X = S
b. X = O



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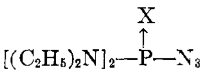
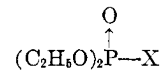
b. X = O



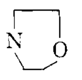
$[(C_2H_5)_2N]_2\overset{X}{\overset{\uparrow}{P}}—N_3$

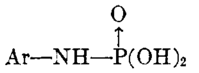
IIIa. X = O
b. X = S



$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}—X$

IVa. X = N_3
b. X = Cl
c. X = NHC_6H_5
d. X =





$Ar—NH—\overset{O}{\overset{\uparrow}{P}}(OH)_2$

Va. Ar = C_6H_5
b. Ar = p-ClC_6H_4

Preparation of a pure sample of a representative thioazide proved difficult—the azide co-distilled with the substituted phosphoryl chloride from which it was prepared—but the chloride–azide mixture showed characteristic azide infrared absorption. The third representative member (IVa) was prepared in high purity, and its infrared data confirmed the open-chain structure.

Reaction of amines with thiatriazoles can result in displacement of an azide moiety and in that respect both the thiatriazoles and carbamyl azides resemble one another.[4] We have investigated whether phosphoryl azides are liable to aminolysis. Thus IVa was refluxed in an excess of aniline for forty hours. After that time clear indication of azide loss was obtained, but no P—O bond rupture (as would be evidenced by the

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[1] (a) Presented in part at the Third Delaware Valley Regional American Chemical Society Meeting, Philadelphia, February, 1960, Abstracts, p. 66; (b) to whom inquiries concerning reprints should be sent. Present address: Chemistry Department, University College, Cork, Ireland; (c) We have used the nomenclature for phosphorus compounds, suggested by the Organic Division of the American Chemical Society and described in *Chem. Eng. News*, **30**, 4516 (1952).

[2] (a) See for example F. L. Scott, *Experientia*, **13**, 275 (1957); see also P. A. S. Smith and D. H. Kenny, *J. Org. Chem.*, **26**, 5221 (1961), for other references. (b) After this work had been presented[1a] and was being written for publication, both diarylphosphonyl azides, see R. K. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961), and imidophosphoryl azides, see H. Boch and W. Wiegräbe, *Angew. Chem.*, **74**, 327 (1962), were found to be acyclic.

[3] L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen & Co., Ltd., London, 1954, chap. 15.

[4] Compare, *e.g.*, F. L. Scott, *Chem. Ind.* (London), 1350 (1956); F. L. Scott, F. C. Britten, and J. Reilly, *J. Org. Chem.*, **21**, 1519 (1956); F. L. Scott and M. T. Scott, *J. Am. Chem. Soc.*, **79**, 6077 (1957).