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MODIFICATIONS OF CELLULOSE: SYNTHESIS AND APPLICATION OF ORGANOPHOSPHORUS COMPOUNDS

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By
Albin Frank Turbak
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MODIFICATION OF CELLULOSE: SYNTHESIS AND APPLICATION OF ORGANOPHOSPHORUS COMPOUNDS

Approved:

Date approved by Chairman: April 22, 1957

DEDICATION

To my son, Stephen

in hoc signo vinces

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ABSTRACT

The purpose of this investigation was to study possible methods of modifying the properties of cellulose, particularly through the use of phosphorus containing compounds. The work covered research in four general areas:

1. attempts to introduce short cross-links into cellulose,
2. attempts to modify the fundamental anhydroglucose units of cellulose,
3. utilization of cellulose as an alcohol function in some of the reactions of phosphorus chemistry, and
4. a study and synthesis of phosphorus-nitrogen compounds for further application to cellulose.

In the course of the investigations of phosphorus compounds, it became necessary to examine the fundamental nature of the phosphoryl linkage. The current literature describing this linkage was critically reviewed and the inadequacy of the $P=O$ symbolism was established. Extensive use was made of the potassium bromide pellet technique in obtaining the infrared spectra of solid compounds.

The attempts to introduce short cross-links included possible diester and aminomethyl ether formation. Cellulose did not react with oxalyl chloride using pyridine catalyst. By reacting cellulose with phosphorus oxychloride at low temperatures using sodium hydroxide catalyst, it was possible to introduce small percentages of phosphorus. The sample so prepared has limited solubility in cupriethylene diamine and was weakened to a greater extent than a sample subjected to the maximum amount of acid that

could be liberated by hydrolysis. This behavior could be attributed to the fact that the phosphorus had formed an internal diester and not a cross-linked product. Cellulose did not react with formaldehyde and diethylamine to produce an alkyl aminomethyl ether under conditions where other alcohols did produce such products.

Two methods were employed in attempts to alter the fundamental structure of cellulose by introducing unsaturation into the anhydroglucose units. The first method employed the preparation of 6-tosyl cellulose, replacement of the tosyl group by iodine, and treatment of the 6-iodo cellulose with silver fluoride in pyridine. This scheme, which had been used successfully to prepare 5,6-glucoseens, was found to be unapplicable to the production of a 5,6-"celluloseen" due to extensive degradation of the cellulose. The second method involved treatment of the cellulose with concentrated potassium hydroxide and carbon tetrachloride. This procedure has been utilized to prepare many olefins, but was found to be unsatisfactory for cellulose and regenerated cellulose.

Cellulose was also employed as an alcohol function in the field of phosphorus chemistry. Phenyl(N-phenyl)phosphonimide, which reacts readily with many hydroxyl containing compounds, had no effect on cellulose. The base catalyzed reaction of halomethylphosphonic acid derivatives was not feasible even under drastic conditions. This lack of reactivity indicated that significant differences exist between carbonyl and phosphoryl structures. Soda cellulose reacted with triphenyl phosphite to yield a product possessing totally new properties and containing 8.58 per cent phosphorus. The phosphorus in this product was not in a trivalent state as evidenced by the lack of reactivity with reagents that are known to alter readily trivalent phosphorus compounds. Trialkyl phosphites did not react well and only low percentages of phosphorus could be introduced. The use of dialkyl hydrogen phosphites in a Todd-type reaction also introduced only small percentages of phosphorus.

The study of phosphorus-nitrogen compounds included both the phosphoramidate and the phosphonamidate type compounds. Phenyldiamidophosphoramidate reacted slowly with aqueous formaldehyde to produce a viscous syrup which displayed film forming properties. Although this syrup did not have any odor of formaldehyde and gave no test for free formaldehyde, it readily liberated formaldehyde on treatment with caustic solutions indicating that it was a reaction product and not some type of hydrolysis product. This phosphoramidate reacted with solid paraformaldehyde in chloroform to produce a solution having film forming properties. Phenyldi(methylamido)phosphoramidate underwent far more facile reaction to produce similar products. The syrup obtained in this case analyzed for 12.9 per cent phosphorus, which was slightly higher than the 11.9 per cent value required for a dimethylol structure. This difference could be accounted for by the presence of some monomethylol compound or by some slight hydrolysis. Phenyldianilidophosphoramidate was found to be unreactive when utilized in the above reaction schemes.

Phenyldiamidophosphonamidate reacted spontaneously and vigorously with aqueous formaldehyde, indicating that the nitrogen atoms on an R-P structure have considerably more amine character than those on an R-O-P structure. The reaction of this phosphonamidate with aldehydes in various solvents demonstrated the unstable nature of the P-N linkage in this compound. If this compound was reacted with aqueous formaldehyde, it was found that both (NH_2) groups were replaced by (OH) groups. By reaction with solid paraformaldehyde in methanol, it was found that one (NH_2) group was replaced by an (OMe) group while use of propanol as solvent caused the replacement of one (NH_2) group or by an (OPr) group. When absolute ethanol was employed as solvent and the reaction was allowed to proceed for 90 minutes at reflux, it was possible to obtain a product having an (OEt) group in place of an (NH_2) group. However, if the reaction was continued for longer periods, it was possible to also isolate a new product having the second (NH_2) group replaced by an (ONH_4) group. Except for ethanol, these reactions would not proceed without the presence of the paraformaldehyde.

In chloroform or carbon tetrachloride where no efficient attacking group was present, the phosphoryl oxygen exhibited an attacking effect to produce a pyro structure. It was further found that paraformaldehyde, benzaldehyde, and propionaldehyde all produced the same product, phenyl(diammonium)pyrophosphonic acid, and that diethyl ketone was incapable of causing reaction to take place. Attempts to synthesize this pyrophosphonic acid derivative by controlled hydrolysis of phenyldichlorophosphine oxide, by reaction of phenyldichlorophosphine oxide with phenylphosphonic acid, by high temperature dehydration, and by reaction of phenylphosphonic acid with urea were all unsuccessful. The assigned phenyl(diammonium)pyrophosphonic acid structure was substantiated by analytical data, spectral data, chemical behavior, and degradation to known products. Phenyldianilidophosphonamidate was found to be unreactive in all of the above-mentioned reaction procedures. This lack of reactivity was due to lower activity of the nitrogen atom and not to solubility effects, since the dianilido compound was more soluble in the solvents than was the diamido compound.

The use of mesomeric structures to explain the behavior of compounds containing a phosphoryl linkage was examined with regard to the known experimental behavior of such compounds. By utilizing the d_{xy} and d_{xz} orbits of phosphorus and noting certain characteristics of these orbits, a concept of the phosphoryl linkage was developed which not only agreed with the observed facts, but could be beneficially employed to predict expected behavior of phosphoryl compounds in various chemical reactions. This concept points out that mesomeric interpretations are inapplicable to phosphoryl compounds since the bent structure of these compounds and the unique directional characteristics of the d orbits makes interaction sterically unfavorable. This concept further demonstrates that fundamental differences exist between phosphoryl and carbonyl structures. Therefore, on the basis of chemical reactivity, physical behavior, and theoretical considerations, it was concluded that the $P=O$ symbolism did not adequately express the true nature of the phosphoryl linkage and should be considered as being incorrect.

CHAPTER I

INTRODUCTION

There has been a considerable amount of work carried out in the field of cellulose chemistry both from the standpoint of cellulose structure and of cellulose modification and derivative formation. Several reference books are available which summarize much of this research (1-4). In spite of this considerable effort, there still exists an urgent need for a cellulose modification which can incorporate such characteristics as resilience, improved strength, and flameproofing in one unique reaction. Processes which tend to produce one of these characteristics usually do so at the expense of other desirable properties or they produce the desired characteristic on a nonpermanent basis.

For example, the use of formaldehyde to improve cellulose recovery (5-7) results in strength losses because of the use of acidic catalysts for the polymerization purposes. Similar results are obtained in the use of glyoxal-, Kaurit-, and urea-formaldehyde type reactions. Cellulose treated with urea or melamine formaldehyde resins further exhibits increased chlorine retention which causes subsequent undesirable changes. It should also be noted that washing causes from 30 to 60 per cent removal of such finishes (8). Such factors bring up rather important questions as to whether these resins are actually chemically combined with the cellulose or are acting in a purely mechanical fashion.

Since resilience and strength are generally associated with crosslinking reactions, it is interesting to note some of the approaches toward cross-linking that have been published. Crotyl cellulose has been cross-linkedby reaction with other unsaturated compounds (9) and also by being subjected to high temperatures which caused opening of the double bond (3,4). Hydroxyethyl allyl ethers have been prepared and cross-linked by the use of peroxide catalyst (10). Allyl ethers of glucopyranose have been subjected to vulcanizing conditons to yield insoluble and infusible products (11). Bridged compounds of cellulose with di-isocyanates have been prepared (12), and a similar reaction involving tri-isocyanates received considerable attention in Germany during World War II for the production of artificial leather for shoes (13). The use of divinyl sulfone as a shrinkproofing agent has also been suggested (14). A rather unusual method which depends on producing succinaldehyde from 2,5 dimethoxytetrahydrofuran, hydrogen chloride, and zinc chloride followed by reacting the succinaldehyde with cellulose has been reported by Walker and Kokowicz (15). The vinylation of cellulose using acetylene and a base catalyst has been investigated, and it is claimed that under drastic conditions it is possible to obtain not only the expected vinyl ethers, but also ethylidene derivatives of cross-chain types (16). Izard and Morgan have utilized the Bunte-type reaction involving cellulose chloroacetate, sodium thiosulfate, and iodine to produce insoluble cross-linked polymers (17). The reaction of carbon suboxide on cellulose has been effected, and it is claimed that such treatments greatly alter the swelling properties of the cellulose (18). Diesters of cellulose and organic dibasic acids, such as phthalic, adipic, and maleic, have also been prepared and studied (19, 20). The use of ethylene ureas formed by the action of ethyleneimine and hexamethylene di-isocyanate has been mentioned. The reaction of these cyclic products with cellulose involves ring opening by the cellulose alcohol function (8).

The above examples indicate that most cross-linking attempts can be included under three main headings:

1. direct linkage due to formation of such compounds as diesters, dicarbamates, diethers, etc.,
2. cross-linkage utilizing an introduced position of unsaturation, and
3. cross-linkage utilizing displacement of halogen functions.

With regard to flameproofing cellulose, attempts to introduce flameproofing properties have been rather unsuccessful because of the nonpermanence of the products. For a long time, impregnation with ammonium phosphate has comprised one of the most generally used approaches to flameproofing cellulose (21). The nonpermanence of the treatment to washing is obvious. During the second world war, Germany introduced the use of sulfamides as additives in resin-formaldehyde treatments to obtain some degree of flame resistance. This process did not prove to be too satisfactory, since the flame resistance was found to be nondurable (22). Work at the Glenn L. Martin Company (23, 24) involving the use of dialkene phosphonamides and brominated alkene phosphates has been reported. It was found that bromine atoms, present as extra structural modifications, were effective flame inhibiting assistants, especially if the bromine atoms were present on adjacent carbon atoms of the alkene phosphate. The fact that halogens can be used for imparting flame resistance has been investigated (25, 26), and it has been established that bromine is more effective than chlorine which in turn is more effective than fluorine. The tetrafluoroethyl ether of cellulose has been prepared and showed some flame resisting qualities (27).

Little (21) has proposed that a flameproofing agent either alters the route of the pyrolytic decomposition to form new incombustible degradation products or releases noncumbustible gases (such as nitrogen, halogen, or sulfur compounds) which form a protective layer around the sample. A mechanism for the burning of cellulose has been put forth (28) in which the first stage of the decomposition involves formation of 1,6 anhydro β-D glucopyranose. This glucopyranose is then said to undergo decomposition to combustible products. It would appear that by blocking the 6 position of cellulose and thus preventing the 1,6 anhydroglucopyranose formation it should be possible to prevent combustion. It was pointed out by Pacsu and Schwenker (26) that all substituents are not equally effective in performing such a task. They found that phosphorylation of the 6 hydroxy group (by the use of diethylphosphorochloridate and pyridine) gave far better results than substitution of the hydroxy group by halogen. However, evidence is readily available to show that a 6-cellulose phosphate itself is not the total answer to flameproofing. The preparation of the monoammonium salt of 6-cellulose phosphate has been reported by Nuessle (29), who used the reaction of urea and phosphoric acid on cellulose in the 130° to 175° C. range. The formation of this ester was further studied by Davis (30), who pointed out that while the monoammonium salt possessed acceptable flameproofing characteristics, the exchange of sodium for ammonium resulted in producing a product possessing virtually no flameproofing action.

The use of organophosphorus derivatives was further investigated at the Southern Regional Research Laboratories where several treatments were devised. The first treatment reported the use of tetrakis(hydroxymethyl)-phosphonium chloride (THPC) prepared by the action of formaldehyde and hydrogen chloride on phosphine (31). This compound was used in conjunction with the regular melamine formaldehyde type products to impart satisfactory flameproofing to cellulose. There are many objections to this procedure some of which include the difficulty of preparation of the phosphonium chloride and the liberation of excessive formaldehyde during processing. A second treatment involved the use of a telomerization procedure between bromoform and triallyl phosphate and was called the bromallylphosphate (BAP) method (32). A third approach involved the use of a phosphonitrilic ester (PNE) which was prepared by the reaction between phosphonitrilic chloride and sodium allylate. This product was then polymerized directly or telomerized with bromoform to produce finishes of a durable nature (33). There is no reason to believe that any of these approaches produce a product that is actually bonded to cellulose.

These examples indicate that most attempts to flameproof cellulose fall into one of three general categories:

1. nonpermanent type treatments,
2. production of cellulose derivatives involving the 6 position of the anhydroglucose units, and
3. utilization of polymeric phosphorus containing compounds.

It is important at this point to note four significant facts with regard to all the work that has been mentioned. First, no specific attempt has been undertaken to produce a short cross-link in cellulose. This is striking since current theory regarding resilience and recovery is based on a chain-slippage hypothesis. It would seem plausible that a short cross-link capable of exerting a restraining effect on the polymeric chains before they began to slip past one another would be more effective than a longer link whose action was felt only after considerable slippage had taken place. Second, no specific attempt has been undertaken to modify the anhydroglucose unit itself for use in further reactions. Any modification of the basic anhydroglucose unit would immediately remove the major restriction which limits cellulose reactions to those specifically requiring an alcohol function. Third, it is apparent that no concentrated effort has been undertaken to determine if cellulose can be used in many reactions of phosphorus chemistry requiring an alcohol function. Fourth, the possibility of using phosphorus-nitrogen compounds to react with cellulose or to produce products of value as cellulose finishes has not been thoroughly investigated. The expected reactions of these systems will be determined by the nature of the phosphoryl linkage. Since there exists considerable inconsistency and uncertainty in the current literature regarding the nature of the phosphoryl linkage, a critical evaluation of the nature of this linkage would be most necessary to an understanding of the behavior of the phosphorus-nitrogen compounds.

This thesis will, therefore, report work which was done in each of the four above-mentioned areas in order to obtain a more fundamental understanding of the reactions involved in cellulose and in phosphorus chemistry. Throughout the work, extensive use will be made of infrared spectral data in ascertaining various structural features.

CHAPTER II

EXPERIMENTAL DISCUSSION

Experimental Work

Cross-Linking Agents.--The introduction of short cross-links into cellulose should theoretically be more advantageous than the introduction of longer cross-links, since the shorter links could exert a restraining effect when the polymeric chains first started slipping rather than after some slippage had occurred. One important point in this respect would be to ascertain what could be the minimum length of a cross bonding link. Haworth and Porter (34) were able to prepare the carbonates of several sugars by using phosgene and careful purifying procedures. The use of higher temperatures produced a gel rather than the soluble carbonate, indicating that the phosgene was forming an intermolecular rather than an intramolecular product. Such action would not necessarily be produced with cellulose since the chains are fixed and not free to move as were the sugar molecules in solution.

Heuser and Schneider (35) have reported the preparation of an alkylated carbonic ester of cellulose. They used a base-catalyzed reaction of methyl chloroformate and obtained a product which was soluble in pyridine and chloroform and was readily hydrolyzed by boiling water to liberate carbon dioxide. Frank and Caro have prepared some oxalyl half esters of cellulose(36). They utilized the oxalyl half acid chloride in pyridine and reported that free oxalyl chloride would not form a stable ester with cellulose.

Since the oxalic acid diester of cellulose would represent one of the shortest possible cross-links, an attempt was made to check the above-reported work. The oxalyl chloride was prepared using the method outlined by Staudinger (37) and was reacted with cellulose using pyridine as the catalyst. All attempts using ester interchange to show that an oxalyl product had formed gave negative results.

Another possible method of introducing short cross-links into cellulose has been claimed by Burges, Leward and Co. (38) which describes the use of phosphorus oxychloride and sodium hydroxide catalyst at moderate temperatures. In a recent investigation, this claim has been shown to be false (39). The use of pyridine as a catalyst for the reaction of phosphorus oxychloride with cellulose and starch has been investigated (39, 40). When pyridine was employed, up to nine per cent phosphorus could be introduced, but the need for fairly high reaction temperatures resulted in cellulose losing approximately 50 per cent of its strength. It was later shown by electrometric titration techniques that from 22 to 60 per cent of the phosphorus introduced was doubly bonded and it was assumed that the second linkage was due to cross-linking (41).

Since the use of the moderate to high temperatures employed in these investigations was considered objectionable, these phosphorylation procedures were repeated using temperatures in the 0° to 2° C. range. The results of some initial experiments are summarized in Table 1. Pyridine catalysis at these low temperatures was insufficient to introduce a significant amount of phosphorus. It should be particularly noted that the solubility of the sample in cupriethylene diamine was drastically affected where even a small percentage of phosphorus was introduced, as in the case

Table 1. Effect of $POCl_3$ Treatment on Cellulose

Treatment	Strength Tests				Phosphorus Content	Viscosity	
	IP_2	Sigma	Ravel Strip	Sigma		Sec[†]	Sigma
	(g.)	(n=40)	(lbs.)	(n=20)	(%)		(n=10)
Original	235.69	37.7	54.14	3.07	---	100.0[a]	0.1
$POCl_3$--Pyr.	220.1[d]	29.6	54.73	5.16	0.06	63.3[a]	0.1
$POCl_3$--Pyr.--Na_2S	229.43	33.2	---	---	none	70.7[b]	0.1
$POCl_3$--NaOH	142.93[e]	54.8	34.66[f]	6.45	0.730	14.0[b]	0.1
$POCl_3$--NaOH-Na_2S	129.61	65.4	---	---	0.097	c	---

[†] 0.5 per cent solutions at 32° C.; mechanical shaker

[a] Completely dissolved in 2 1/2 hours

[b] Some particles left undissolved after five hours

[c] Did not dissolve to any appreciable extent even after five hours

[d] Insignificantly different; "t" level less than three

[e] Significantly lower than standard; "t" level equals 8.83

[f] Significantly lower than standard; "t" level equals 13.16

of sodium hydroxide catalysis. Of equal importance is the fact that the samples became even more insoluble on treatment with sodium sulfide in warm ethylene glycol. The samples so treated lost most of their phosphorus content and no bound sulfur could be detected.

The effects of temperature, sodium hydroxide concentration, and time of phosphyorylation on the cellulose strength were further investigated and the results are given in Table 2. This table shows that the treatment of cellulose with sodium hydroxide and the maximum amount of hydrogen chloride that could be produced by hydrolysis gave a higher breaking strength than a similar treatment where phosphorus oxychloride was used. This fact suggests that factors other than acid hydrolysis are important.

A third possible method for introducing short cross-links was also investigated. The reaction of amines with formaldehyde and alcohols in the presence of potassium carbonate to produce alkyl aminomethyl ethers and diethers has been reported (42, 43). These products appear to have reasonable stability to hydrolysis if the alcohol function has a high molecular weight. In an attempt to determine the reactivity of alcohol groups in cellulose toward this reaction, diethylamine and formaldehyde were reacted with cellulose in the presence of potassium carbonate. The resulting sample analyzed for 0.2 per cent nitrogen and, thus, it was evident that the expected cellulose diethylaminomethyl ether did not form in appreciable amounts.

<u>Attempts to Modify the Anhydroglucose Units</u>.--In reviewing the literature it becomes rapidly apparent that practically all of the reactions attempted by the many investigators have been additions utilizing the basic anhydroglucose alcohol functions. If the basic structure could possibly be

Table 2. The Effects of Various $NaOH-POCl_3$ Treatments on Cellulose

Treatment[†]	Single End Strength	Standard Deviation	Per Cent Phosphorus	Tests (n)	Temperature (°C.)	Time (hrs.)
Padded with NaOEt-0.2 moles $POCl_3$	129.62	16.1	1.7	37	15	1
Same as above	127.68	14.2	1.7	41	15	2
Padded with 20% NaOH-0.2 moles $POCl_3$	151.7	15.6	2.17	43	15	1
Same as above	123.3	14.7	2.2	41	15	2
Padded with 4% NaOH-0.2 moles $POCl_3$	222.0	24.1	0.41	38	-2 ± 2	2
Padded with 20% NaOH only	211.98[b]	26.9	--	50	-2 ± 2	1
Same as above	184.9[b]	15.3	--	43	-2 ± 2	2
Padded with 20% NaOH-0.2 moles $POCl_3$	133.9[a]	13.9	2.3	42	-2 ± 2	1
Same as above	114.2	12.1	2.8	42	-2 ± 2	2
Padded with 20% NaOH-0.6 moles HCl	163.7[a]	18.9	--	46	-2 ± 2	1
Original	230.5	29.1	--	36	--	-

[†] All treatments performed with 150 ml. of carbon tetrachloride

[a] "t" level for these means equals 8.53

[b] "t" level for these means equals 5.8

altered without degrading the polymer considerably, then it would be possible to apply many new reaction schemes. One such modification of the basic structure could involve the introduction of a double bond.

The reaction of 6-iodo glucose with silver fluoride in pyridine to give a 5,6-glucoseen (unsaturated 5,6 position) has been established (44-47). Since this reaction had not been reported for cellulose and since a 5,6-celluloseen would be an extremely interesting and valuable product, it was decided to attempt this preparation. Tosyl cellulose was prepared according to methods described in the literature (48-50), and the sulfur content of the sample indicated the presence of one tosyl group for every two anhydroglucose residues. The 6-iodo cellulose was then prepared by the well-known method involving the use of sodium iodide in acetone (51, 52) Silver fluoride was prepared by the method of Mellor (53). The 6-iodo cellulose was then shaken for 40 hours at room temperature with silver fluoride dissolved in excess pyridine. At the end of this 40-hour period, the cellulose was converted into a completely black solution, and the flask was covered with a metallic silver deposit. The black solution could not be characterized further.

Another possible method for introducing double bonds into cellulose was also investigated. The use of chloroform reacting with both primary and secondary alcohols in strong potassium hydroxide to produce olefins has been reported (54). The yields of olefin renged from 7 to 35 per cent with the various alcohols; cyclohexyl and secondary butyl alcohols yielded 14 and 34 per cent, respectively. If such a technique did introduce a double bond into cellulose, the double bond might form at the 1,2 position to yield a ketene acetal, at the 3,4 position to yield a vinyl ether, at the

5,6 position to yield a 5,6-celluloseen, or at the 2,3 position to yield a vinyl alcohol which could undergo tautomerization to form either a 2 or 3 keto cellulose. Using the recommended procedure, a sample of cotton linters was added to a strong potassium hydroxide solution and refluxed while the chloroform was added dropwise. In a second procedure, the cellulose was first dissolved in cupriethylene diamine and reprecipitated by use of sulfuric acid to give a regenerated cellulose of very open structure to facilitate reaction. None of the samples thus treated decolorized bromine solutions visibly and gave subsequent negative sodium fusion and displacement tests for the presence of bromine.

Reaction of Cellulose with Phosphorus Containing Compounds.--In this phase of the investigation an effort was made to ascertain the behavior of cellulose in reactions with phosphorus compounds requiring an alcohol function.

The nomenclature used throughout this thesis is that proposed by the American Chemical Society. Compounds are named as derivatives of their corresponding parent acids; those having no C - P bond being phosphoric derivatives, those having one C - P bond being phosphonic derivatives, and those having two C - P bonds being phosphinic derivatives. The presence of other functions such as nitrogen or chlorine is further indicated by such terms as "amidate" and "chloridate", respectively, used in conjunction with the above-mentioned terminology.

Phosphonimides can be prepared by the reaction of phosphonyl dichlorides with amine hydrochlorides. The compound actually employed was phenyl-(n-phenyl)phosphonimide which was prepared by the reaction of phenyldichlorophosphine oxide and aniline hydrochloride according to the method of Michealis (56). This compound was then reacted in chloroform solution with cellulose in the hope of producing PhP(O)(OCell)(NHPh). Analysis of the sample after reaction showed that essentially no phosphorus had been introduced. The phosphonimides are generally written so as to indicate the presence of a double bond between phosphorus and nitrogen and facile reactions of these compounds with alcohols have, indeed, been pictured as addition reaction (55). Actually, these phosphonimides have been shown to exist as dimers by molecular weight values. The ease of reaction could also be explained as being caused by the opening of an unstable four membered P - N ring system.

Attention was then centered on the possibility of reacting cellulose with halomethyl phosphonic acid and its derivatives. The free acid represents the phosphorus analogue of chloroacetic acid and, since chloroacetic acid reacts rather readily with cellulose, it was expected that the chloromethylphosphonic acid would show a similar behavior. Of all the halogens, iodine behaves as the best leaving group in nucleophilic-type displacement reactions (57). Therefore, a base-catalyzed reaction between cellulose and an iodomethylphosphonic acid derivative was attempted. In performing this reaction, iodomethyldiethylphosphonate was prepared using a Michealis-Arbusov type reaction between methylene iodide and triethyl phosphite (58, 59). The reaction of iodomethyldiethylphosphonate was performed using both sodium hydroxide and pyridine as catalysts and employing temperatures ranging from room temperature to 110° C. baking conditions in an oven. The samples treated in this manner were found to contain no phosphorus.

It was thought that the relative insolubility of iodomethyldiethylphosphonate in water could be the factor which was limiting the reaction.

To investigate the validity of this assumption, cellulose was treated with sodium hydroxide and chloromethylphosphonic acid using a procedure described by Reinhardt and Reid (60) for the laboratory preparation of carboxymethylcellulose. A portion of the sample thus prepared was then subjected to rather severe baking conditions. A second procedure employed the use of excess pyridine catalyst at both low and high temperatures. Analyses of these samples showed that they contained no phosphorus. The use of chloromethyldiethylphosphonate produced similar results.

A third section of this phase of the research dealt with investigating the use of cellulose in transesterification reactions involving phosphites. It has been reported by Milobendzki (61) that propanol reacts with triphenyl phosphite at elevated temperatures to produce propyldipropylphosphonate rather than the expected tripropyl phosphite. This type of isomerization product was also reported for methanol. If sodium alcoholates were employed, however, the expected phosphite-type products were observed. Cellulose was first heated at 165° C. in pure triphenyl phosphite. In a second procedure, cellulose was heated in excess triphenyl phosphite at 240° C. in a flask fitted to allow for distillation of any phenol, while a third procedure involved the use of pyridine catalyst. No phosphorus was introduced into any of these samples. The reaction of soda cellulose with triphenyl phosphite at moderate temperatures, however, produced a cellulose product which contained 8.58 per cent phosphorus and displayed most unusual properties. A sample prepared in this manner resembled normal cellulose when washed in alcohol and acetone, but became extremely gelatinous and very translucent when wetted in water. The gelatinous texture could not be attributed to the presence of excess caustic since a sample would not yield a basic solution. The gelatinous texture disappeared when the sample was washed with acetone to remove the water but reappeared when the cellulose was again placed in an aqueous medium. Triphenyl phosphite and other trivalent phosphorus compounds react readily with iodine solutions, sulfur suspensions, and hydrogen peroxide (62, 63) yet the cellulose phosphite would not undergo any of these reactions even when heated. This product was also stable to boiling in water, in 20 per cent acetic acid, and in eight per cent potassium carbonate. On standing in the atmosphere for extended periods of time, the sample lost most of its gelatinous texture and translucence even though it retained its phosphorus content. Hot sodium hydroxide solutions were capable of causing a decrease in the phosphorus content. Phosphorus could be introduced only if undiluted triphenyl phosphite was employed for treating the soda cellulose. Thus, refluxing a sample of soda cellulose for extended periods in a 60 per cent by volume solution of triphenyl phosphite in carbon tetrachloride failed to introduce any phosphorus.

Subsequent to this work, discussions with Dr. I. Hechenbleikner of Shea Chemical Company established that the phosphited cellulose could undergo hydrolysis to produce a P - OH linkage. Such linkages rearrange readily to H - P(O) structures which would not exhibit any of the properties commonly ascribed to trivalent phosphorus compounds. This hypothesis explains some of the characteristics observed for the reaction product.

A further extension of this work to the use of alkyl phosphites was attempted. It has been reported that alcohols undergo uncatalyzed transesterification with trialkyl phosphites (64). A sample of cellulose heated at 140° to 150° C. in excess triethyl phosphite for two days was found to be unaffected. The use of soda cellulose effected an introduction of small amounts of phosphorus. It was also found that pyridine was not a satisfactory catalyst. The use of trimethyl, tributyl, or triallyl phosphites in place of the triethyl phosphite produced essentially the same results.

The use of dialkyl hydrogen phosphite, carbon tetrachloride, a tertiary amine and an alcohol to produce trialkyl phosphates has been reported by Todd (65) and is recommended as a mild phosphorylation procedure. This reaction was further studied by Steinberg (66) who gave evidence for the formation of a phosphorochloridate as an intermediate. This reaction was applied to cellulose using dimethyl hydrogen phosphite and pyridine dissolved in carbon tetrachloride solvent. This cellulose product was found to have a 1.78 per cent phosphorus content.

Reactions of Phenyldiamidophosphoramidates with Formaldehyde.--There are many commercially useful products which utilize urea- or amide-type compounds as intermediates. The urea resins and the pyridinium salts of chloromethyl amides constitute two significant examples of importance to the textile field (67). Both of these examples involve also the reaction of the amide with formaldehyde somewhere in their reaction schemes. The reaction of formaldehyde with the amides of acids other than carboxylic acids has received little study. Mc Masters' investigation of the reaction of *para*-toluene sulfonamide with formaldehyde to give methylene bridged compounds of a cyclic and a linear nature is one of the few examples to be found in the literature (68). The fact that carboxylic amides react with formaldehyde to yield methylols while amines generally react to yield Schiff-type bases is intimately related to the interaction of the carbonyl group with the unshared pair of electrons on the nitrogen atom (69).

A study involving similar reactions with amides of phosphorus acids could possibly produce valuable information regarding the character of the molecular structures present.

Since no information could be found describing a study of phosphorus-nitrogen compounds with formaldehyde, an investigation of such a reaction was made using phenyldiamidophosphoramidate. This compound was prepared using the method described by Audrieth and Toy (70) and was reacted with both formalin in water solvent and with paraformaldehyde in chloroform solvent. The reaction with aqueous formaldehyde did not proceed at any appreciable rate at room temperature and most of the starting compound could be recovered unaltered even after extended periods of standing. When the reaction was heated, however, the phosphoramidate went into solution in about 15 minutes. On cooling such solutions, it was possible to obtain a syrupy product which was very soluble in chloroform and produced clear films when the chloroform solvent was removed. Upon refluxing the phenyldiamidophosphoramidate with paraformaldehyde in chloroform, solutions were obtained which produced clear films on evaporation of the solvent. On prolonged standing these solutions produced small amounts of a white solid. However, although these reactions were extended over 63 hours refluxing, they produced only very small amounts of the white solid. The significant difference noted was that the films produced from the liquor in this case were more waxy.

This investigation was then extended to include phenyldi(methylamido)-phosphoramidate as well as phenyl dianilidophosphoramidate, both of which were prepared by methods described in the literature (71). While the phenyldianilidophosphoramidate did not react with formaldehyde under any of the previously described conditions, the phenyldi(methylamido)phosphoramidate reacted very readily. The presence of the methyl groupings appeared to enhance reaction significantly since the dimethyl compound went into complete solution in aqueous formaldehyde after 15 minutes shaking at room temperature. By evaporation of the water, it was possible to obtain a syrup which appeared and behaved very similar to the one obtained from the diamido compound. This syrup contained 12.9 per cent phosphorus and did not possess the characteristic odor of formaldehyde. The phosphorus analysis is slightly higher than the 11.9 per cent required for a dimethylol compound and could suggest either the presence of some monomethylol product or the presence of some acidic hydrolysis components. The dimethyl compound also reacted more readily with paraformaldehyde in chloroform requiring only 30 minutes' reaction time at reflux as compared with three hours for the diamido compound. These chloroform solutions also displayed film forming properties on evaporation of the excess solvent. The extreme ease with which these products formed films made it difficult to obtain a sample sufficiently pure for analysis and was responsible for extension of these reactions to the corresponding phosphonamidates.

When the phenyldiamidophosphoramidate was reacted with paraformaldehyde in pyridine, it was possible to obtain a complete solution which, on reaction with pyridine hydrochloride, produced relatively large amounts of a white solid product. This product was insoluble in most solvents but dissolved very readily in cold water. It was purified from water solution by precipitation with excess acetone and was found to contain large percentages of nitrogen and chlorine but no phosphorus. The infrared spectrum of this solid displayed only one pronounced absorption band in the region where ammonium structures would absorb. This solid was not investigated further but, on the basis of later work with phosphonamidates, it appears that this product was impure ammonium chloride produced by cleavage of the starting compound.

Reaction of Phenyldiamidophosphonamidates with Carbonyls.--The difficulty experienced in trying to obtain pure compounds from the Ph - O - P compounds led to extension of the investigation to the analogous Ph - P type derivatives. These series represent what might well be considered as the phosphorus analogues of urea. The phenyldiamidophosphonamidate and the phenyldianilidophosphonamidate were prepared by the method of Michealis (72). In contrast to the diamidophosphoramidate, the reaction of the diamidophosphonamidate with aqueous formaldehyde was spontaneous and very vigorous, raising the reaction temperature from 25° to 60° C, and going to completion in a matter of minutes. If the reaction was kept at room temperature by cooling, it produced the same product in about 20 minutes. The product was isolated by evaporating the excess liquor and recrystallizing the resulting solid from hot 95 per cent alcohol. This product was shown by analysis, infrared spectral comparison, and independent synthesis to be monoammonium salt of phenylphosphonic acid. To demonstrate the hydrolysis caused by water alone was not the determining factor, an experiment was performed without the presence of formaldehyde. After the solution stood at room temperature for five days, it was possible to recover essentially all of the starting phosphorus compound. It should be mentioned in this regard that the aliphatic analogues do not possess this stability to hydrolysis and methyldiamidophosphonamidate hydrolyzes to the monoammonium salt of methylphosphonic acid on exposure to atmospheric moisture (73).

The reaction of phenyldiamidophosphonamidate with paraformaldehyde in chloroform was found to be interesting. Since neither of these two starting materials was either water or chloroform soluble, it was quite surprising to find that the two solids when stirred and refluxed for 12 hours produce a third solid which was insoluble in chloroform but extremely water-soluble. This product was recrystallized from 95 per cent alcohol to yield long needle-shaped crystals. A 10 per cent solution of these crystals in water was found to be neutral to litmus even though analysis showed the presence of a 1:1 ratio of phosphorus to nitrogen. One of the few structures capable of exhibiting such behavior would be phenyldiammoniumpyrophosphonate, and the complete analysis of the crystals was found to be consistent with this proposed structure. The crystals formed precipitates of heavy metal salts readily, and it was found further that in forming the silver salt, the compound had lost its entire nitrogen content. An unusual thing occurred in attempting the acid hydrolysis of this compound in that the addition of concentrated hydrochloric acid to a water solution caused the formation of a precipitate. This precipitate was found to contain no nitrogen and exhibited an interesting melting point phenomenon. If the melting determination was started at room temperature, the compound appeared to sinter somewhat and finally melted at 208° C. On the other hand, if the compound was placed in the bath at a temperature above 123° C., it melted immediately. As the temperature was further increased, it resolidified and finally remelted at 208° C. Pure phenylphosphonic acid did not give any precipitate under the conditions employed for obtaining this product. If the precipitated product was allowed to remain in an acid solution overnight, a clear solution was obtained which on evaporation produced only pure phenylphosphonic acid, the expected cleavage product for phenylpyrophosphonic acid. Independent syntheses of phenyldiammoniumpyrophosphonate were attempted. Several experiments involving the controlled hydrolysis of phenyldichlorophosphine oxide and the reaction of phenyldichlorophosphine oxide with phenylphosphonic acid proved unsuccessful. The preparation of phenylpyrophosphonic acid by heating phenylphosphonic acid was reported by Michealis (74). He did not characterize this product, and it is believed on the basis of spectral similarities that the glassy state solid obtained by this heating procedure is not the desired product but a metastable physical form of phenylphosphonic acid. A final attempt to prepare the desired pyrophosphonate involved the use of a novel procedure described by Davis, Findley, and Rogers (30). While investigating the mechanism of the urea-phosphoric acid method of phosphorylating cellulose, they provided evidence to show that diammonium pyrophosphate was formed as one of the products. An experiment was performed using phenylphosphonic acid in place of the phosphoric acid, but none of the desired product could be isolated from the reaction mixture.

To illustrate that the reaction of the phenyldiamidophosphonamidate with paraformaldehyde was not effected by solvent, the phosphorus compound was treated for extended periods in chloroform only. It was possible to recover essentially all of the starting compound. Further, it was found that diethyl ketone was not capable of effecting the reaction. A most interesting point is that both benzaldehyde and propionaldehyde could take the place of the paraformaldehyde as catalyst for the reaction. It was shown conclusively by mixed melting point and infrared spectra that the same compound was obtained regardless of which of these aldehydes was employed.

The use of ethanol as a solvent for the reaction of phenyldiamidophosphonamidate with paraformaldehyde was investigated. The reaction mixture yielded a clear solution in 90 minutes, and subsequent evaporation of the liquor obtained by stopping the reaction at this point gave a white solid. By extracting this solid with successive portions of hot carbon tetrachloride, it was possible to isolate a crystalline product whose analysis and infrared spectrum were consistent with that expected for phenylethylphosphonamidate. The structure of this product was established by separate synthesis. Phenyldiethylphosphonite was prepared and chlorinated to produce some phenylethylphosphonochloridate by way of a Michealis-Arbusov type reaction. This phosphonochloridate was not isolated but dropped directly into liquid ammonia to give the same product as obtained above.

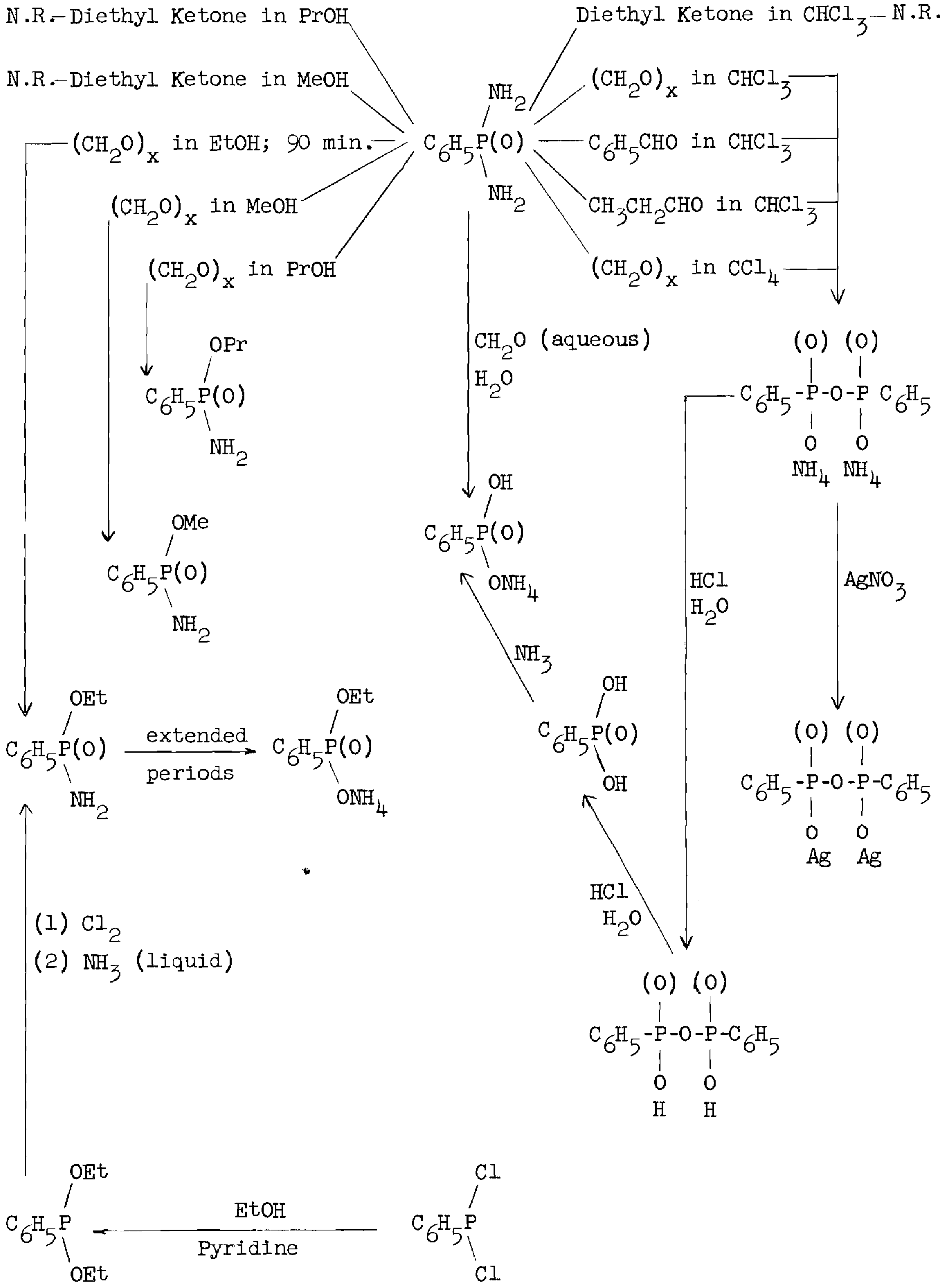
When the above reaction was not stopped after 90 minutes but allowed to continue for 3 hours or more, it was possible to also isolate a new product. This product had an analysis and an infrared spectrum which was consistent with that expected for phenylethylammoniumphosphonate.

The use of methanol as a solvent for the reaction was also investigated. By utilizing identical procedures, it was possible to isolate a compound whose analysis and spectrum were consistent with that expected for phenylmethylphosphonamidate. Extension of the reaction to the use of propanol was also investigated, and the product isolated in this case had an analysis and infrared spectrum consistent with that expected for phenylpropylphosphonamidate.

The pure alcohols and alcoholic solutions of diethyl ketone were investigated to determine their effects on the reaction. In the case of ethanol, it was observed that the same product could be obtained without the specific use of paraformaldehyde when the reaction was allowed to proceed for extended periods, but both methanol and propanol required that it be present for the reaction to proceed. For example, methanol yielded no product on being refluxed for 48 hours with the phosphorus compound but, if the paraformaldehyde was added, then the reaction was completed in 100 minutes at reflux.

All of the above-described procedures for the reaction of phenyldiamidophosphonamidate were repeated using phenyldianilidophosphonamidate. In these cases, very good yields of starting compound could be recovered and so it was concluded that the presence of the added phenyl groups had a pronounced deactivating effect on the reaction. The lack of reactivity could not be attributed to solubility characteristics, since the dianilido compound was more soluble in most of the solvents than was the diamido compound.

The following reaction summary outlines the reactions of phenyldiamidophosphonamidate.



N.R.–Diethyl Ketone in PrOH
N.R.–Diethyl Ketone in MeOH
(CH$_2$O)$_x$ in EtOH; 90 min.
(CH$_2$O)$_x$ in MeOH
(CH$_2$O)$_x$ in PrOH
Diethyl Ketone in CHCl$_3$–N.R.
(CH$_2$O)$_x$ in CHCl$_3$
C$_6$H$_5$CHO in CHCl$_3$
CH$_3$CH$_2$CHO in CHCl$_3$
(CH$_2$O)$_x$ in CCl$_4$
C$_6$H$_5$P(O)(NH$_2$)$_2$
C$_6$H$_5$P(O)(OPr)NH$_2$
C$_6$H$_5$P(O)(OMe)NH$_2$
CH$_2$O (aqueous)
H$_2$O
C$_6$H$_5$P(O)(OH)ONH$_4$
NH$_3$
C$_6$H$_5$P(O)(OH)OH
(O) (O)
C$_6$H$_5$-P-O-P C$_6$H$_5$
O O
NH$_4$ NH$_4$
AgNO$_3$
C$_6$H$_5$-P-O-P-C$_6$H$_5$
Ag Ag
HCl
H$_2$O
C$_6$H$_5$-P-O-P-C$_6$H$_5$
H H
C$_6$H$_5$P(O)(OEt)NH$_2$
extended
periods
C$_6$H$_5$P(O)(OEt)ONH$_4$
(1) Cl$_2$
(2) NH$_3$ (liquid)
C$_6$H$_5$P(OEt)$_2$
EtOH
Pyridine
C$_6$H$_5$PCl$_2$

Theoretical Discussion

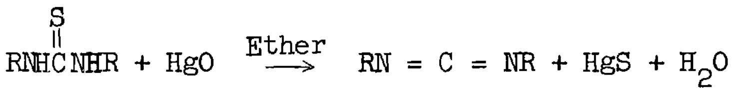
There are points of theoretical interest that should be discussed in each of several areas involved in this work.

Action of Phosphorus Oxychloride on Cellulose.--The fact that phosphorylation of cellulose with pyridine at high temperatures results in a major decrease of strength has previously been noted (39) and similar decreases on phosphorylation with sodium hydroxide at low temperatures are mentioned in this report. There is no reason to suspect that the products obtained by both of these base-catalyzed reactions would not be similar. It has been demonstrated quite conclusively (41) by electrometric titration that, for phosphorylation using pyridine, from 22 to 60 per cent of the phosphorus is doubly bound. It is shown in this work that the cellulose which is phosphorylated is definitely weaker than a similar sample which has been exposed to the maximum amount of hydrogen chloride which could be liberated. If the doubly-bound phosphorus is present in any amount as a cross-linkage, there is no reason to suspect that introducing phosphorus would produce a weaker sample. A correlation of all these results appears in an interpretation of the insolubility of the phosphorylated cellulose in cupriethylene diamine.

The solubility of cellulose in cupriethylene diamine has been investigated (75-77). The actual mechanism of the solvation was established by Reeves (78, 79) who studied the reaction of copper complexes with compounds having adjacent hydroxyls whose angles were fixed by ring systems. He showed that the 2- and 3-hydroxyls of cellulose would be involved in the solution process. The apparent conclusion to be drawn from this work is that insolubility of cellulose could come from cross-linkage between polymeric chains or, of equal importance, could arise as a result of blocking either the 2- or 3-hydroxyl position. The facts that cellulose contains phosphorus which is doubly bound to a great extent, that it is insoluble in cupriethylene diamine, and that it is considerably weaker can then readily be reconciled by involving at least the partial formation of a cyclic internal diester between the 3 and 6 positions of the anhydroglucose unit.

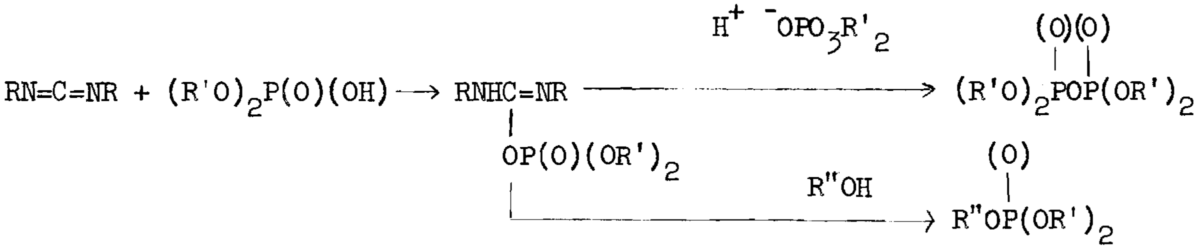
The Urea-Phosphoric Acid Reaction.--The reaction of urea with phosphoric acid to produce a 6-cellulose monoammonium phosphate has been described (29). Investigation of the reaction in the absence of cellulose led to the isolation of diammonium pyrophosphate and cyanuric acid as two reaction products (30). The actual mechanism of the phosphorylation was not conclusively established by this work. The investigators pointed out that although it was possible to introduce phosphorus by use of the pyrophosphate which was formed, the amounts that could be introduced were far less than those actually introduced in the original process. The direct relation of this reaction to the work of this thesis was its application as a possible method of synthesizing phenyldiammoniumpyrophosphonate. Several reasons may be advanced for expecting this extension to be valid.

Some biological synthesis work (80-83) allows a very reasonable mechanism to be proposed for the earlier processes. Todd and his associates have reported several methods of mild phosphorylation for preparatory use in studying nucleotides. One of these methods provides a unique synthesis of phosphorus compounds and involves the use of carbodiimides. Substituted carbodiimides can be prepared by the reaction of the corresponding substituted thiourea with mercuric oxide (84).



$$RNH\overset{\overset{S}{\|}}{C}NHR + HgO \xrightarrow{Ether} RN = C = NR + HgS + H_2O$$

The reaction of carbodiimides with carboxylic acids to produce anhydrides has been investigated by Zetzsche (85). Todd and others extended the reaction to include the synthesis of pyrophosphates from both mono and dihydrogen phosphates. It was also applied to the production of cyclic phosphates from glycol monophosphates. Their proposed mechanism is



$$RN{=}C{=}NR + (R'O)_2P(O)(OH) \longrightarrow \underset{OP(O)(OR')_2}{RNHC{=}NR} \xrightarrow{H^+\ ^-OPO_3R'_2} (R'O)_2\overset{(O)(O)}{POP}(OR')_2$$

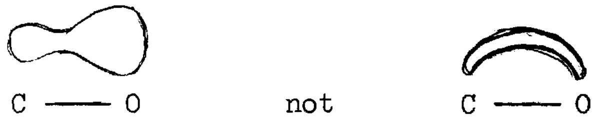
$$\xrightarrow{R''OH} R''O\overset{(O)}{P}(OR')_2$$

The supposition that urea forms some type of C = N structure on being melted is not unreasonable and is the only requirement necessary in extending the above mechanism to offer new and useful explanation for the urea-phosphoric acid process of producing 6-cellulose monoammonium phosphate. Furthermore, it is proposed that thiourea would be more beneficial than urea and that acids other than ortho phosphoric acid could be employed to obtain a whole range of different phosphorus-cellulose products. The reason why phenylphosphonic acid did not produce the desired phenyldiammonium pyrophosphonate could then be attributed to the inefficient action of urea as compared to carbodiimides.

The Nature of the Phosphoryl Linkage.--An understanding of the nature of the phosphoryl linkage is of paramount importance in predicting expected behavior patterns for phosphorus compounds under different reaction conditions. There is a considerable amount of dispute in the current literature regarding the nature of the phosphoryl oxygen, both from the standpoint of a correct interpretation of its electronic structure and of its effect on the chemical reactivity of compounds. There are two main schools of thought, one of which envisages a coordinate covalent $P^+ - O^-$ bonding and the other favors resonance contributions as expressed by a $P = O$ symbolism. However, there is only one phosphoryl linkage and only one correct interpretation, whether it involves a compromise of both models or whether it favors one postulate over the other. It can be assumed that the model which is most closely in agreement with recent experimental facts should be utilized as being most representative of the situation.

In the first place, it is essential that the double bond symbolism in chemistry be reviewed as to its meaning and intended usage. The double bond symbolism was originally designed to express what is recognized now as an interaction of _p_-type electrons in unsaturated hydrocarbon compounds. It should be noted that here the unsaturation is between like atoms where no difference or only minor differences in electronegativity exist. A general extension of the double bond symbolism to heteronuclear diatomics was evolved with minimum attention and stress being given to the fact that important differences now were present (86). These differences are somewhat pointed out by the organic chemists' current use of arrows to represent the situation that adherents to the valence bond school describe as percentage of ionic character (for example, $>C^{\delta\oplus} \overset{\curvearrowright}{=} O^{\delta\ominus}$).

In the second place, there is justified criticism of the currently accepted $C = O$ notation. With reference to the description of this carbonyl grouping in terms of percentage of ionic character and valence bond structures, the usually accepted interpretation (87) is that the linkage is C = O with about 50 per cent $C^+ - O^-$ ionic contribution. It is, perhaps, appropriate at this point to draw a pointed analogy with regard to the above statement. If a chemist has some pure alcohol and begins to dilute it with water, how long is he entitled to call the resulting liquor a solution of water in alcohol and when should be begin to call it a solution of alcohol in water? If one allows the 50 per cent point to represent an acceptable limit, then compounds having more than this amount of ionic character would be more correctly described as ionic structures which are modified by double bond character. Coulson (88) has pointed out that the *pi*-electron distribution of carbonyls is best pictured as having the shape of a ping pong paddle with the larger end over the oxygen atom rather than the usual symmetrical distribution associated with hydrocarbon unsaturation. For example,



It appears from these arguments that oxygen is not anxious to share its electrons with a neighbor and generally will do so only partially.

Since the preparation of so-called pentavalent phosphoryl compounds generally involves the utilization of the unshared pair of electrons of trivalent phosphorus, a brief review of some of the reactions and characteristics of trivalent phosphorus compounds is pertinent to this discussion. The phosphorus trihalides are convenient compounds to consider first since the X - P - X bond angles increase directly with the electronegativity of the halogen atom. The arguments put forth by Cartmell and Fowles (89) should be considered in proposing an explanation for bond angle differences.

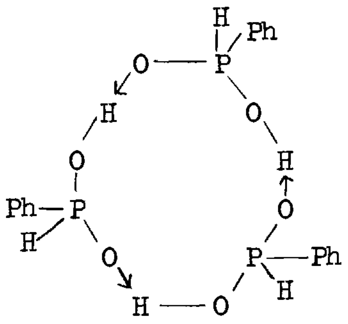
In attempting to explain why NH_3 has larger bond angles than NF_3, they propose that the bonds involved are of the sp^3 type and that the NF_3 bonds have more p-character, exclusively due to the fact that the fluorine atom is more electronegative than is the hydrogen atom. Then they extend this argument to phosphines and arsines pointing out that the P - H linkage, which also involves sp^3 type bonds due to hybridization of the 3s and 3p orbits, would have more p character than the N - H linkage because of the lower electronegativity of phosphorus compared to nitrogen. This explanation appears to solve the problem of the 106 degree angles for NH_3, the 102 degree angles for NF_3, and the 94 degree angles for PH_3 except for one rather important point. If one extends this argument to PF_3, it would be necessary to predict angles of 90 degrees corresponding to almost pure p bonding. Actually the PF_3 angles are about 106 degrees and so it appears that such explanations are not as comprehensive as they may appear. On the other hand, Van Wazer (90) has proposed an explanation for the angles of phosphorus trihalides which is diammetrically opposite to that of Cartmell and Fowles. He proposes that sp^3 hybridization occurs and that more s character should be invoked as the electronegativity is increased. Obviously, while this argument holds for phosphorus, it cannot be applied to the analogous nitrogen compounds for it predicts the wrong answers.

Above and beyond either of these hypotheses, it should be pointed out the phosphorus atom is fairly large and should be readily polarizable. On this basis, a good correlation for most of the properties and reactions can be obtained. Not only can the direct correlation of bond angles with electronegativity be made, since highly electronegative atoms maintain rather high charges, but also this picture is consistent with the nucleophilic behavior exhibited by these compounds. Although nucleophilicity is in general related to basicity, it does not necessarily follow that a strong base will be a good nucleophile. This is true because basicity represents an equilibrium or thermodynamic concept whereas nucleophilicity represents a rate value. Trivalent phosphorus compounds are good nucleophiles and most of their reactions can be considered to involve nucleophilic attacks. The general availability of electrons on phosphorus decreases as (RO) groups are substituted for (R) groups indicating that simple inductive effects are dominant. This is strikingly demonstrated in considering that $(RO)_3P$ compounds react with sulfur only if heated, while $RP(OR)_2$ compounds react spontaneously and R_3P compounds react rapidly and completely enough to be used as titration reagents for sulfur (91, 92, 63). This indicates that substitution of (R) by (RO) diminishes the electron availability by an inductive effect rather than increasing it by a mesomeric effect. Bartlett (63) has pointed out that the reaction is accelerated by electron releasing groups and is as sharply dependent on solvent as quarternary salt formation in which the transition state is considered to be 50 per cent separated into ions. It appears then that in using its unshared pair of electrons, phosphorus is not reluctant to accept a positive charge. Another example of the nucleophilic nature of trivalent phosphorus compounds involves the use of trialkyl phosphites reacting with *para*-toluenesulfonic esters to yield phosphonic acid derivatives (93). This behavior is in agreement with the generally accepted reactions of nucleophilic reagents. A similar reaction has been reported involving displacement of the nitrogen structures of Mannich bases (94). A further important example of the use of the free electrons is found in the well-known

Michialis-Arbusov transformation where phosphites have been reacted with a great variety of alkyl and acyl halides to give rearranged phosphonic acid derivatives. Mechanistically, this reaction has been visualized in this work as involving attack by the phosphorus to form a quarternary-type compound, ionization to give an anion, and subsequent S_n2 attack by the anion on one of the (R) groups originally present in the P - O - R compound. In support of these hypotheses are the facts that quarternary intermediates have been isolated and that inversion takes place if an optically active phosphite prepared from optically active 2-octanol is used (95, 96). Again it is to be pointed out for this reaction that substituting (RO) or (Cl) for (R) drastically lowers the reaction rate. Although acyl halides, carbamyl halides, and acid anhydrides have all been successfully reacted by the Michealis-Arbusov scheme, sulfonyl halides do not react or else form compounds which are very unstable and decompose before they can be isolated (97). The nature of the sulfonyl and phosphoryl linkages appears to be involved in this case, since other sulfur compounds react as expected.

These examples of the reactions of trivalent phosphorus compounds have been presented to illustrate the role that the free electrons play in reactions and to point out that their availability is directly related to the inductive nature of the groups attached to the phosphorus atom. If resonance effects were important then substitution of (RO) groups for (R) groups should enhance reaction rather than inhibit it. These effects follow such a characteristic pattern that the reactivity of the unshared electrons can be predicted to decrease in the order $R_3P > R_2P(OR) > RP(OR)_2 > (RO)_3P$.

In extending this pattern to include phosphoryl compounds, the similarities are very striking. The phosphoryl oxygen is quite polar as is readily evidenced by its ability to undergo strong hydrogen bonding. For example, phenlyphosphinic acid is known to exist as a trimer in benzene



solution (98) and the phosphoryl-oxygen stretching band in the infrared region is considerably shifted whenever opportunities for hydrogen bonding are present (99). Geddes (100) has presented spectral data for the interaction of phosphoryl oxygen with alcohols showing that the phosphoryl oxygen of $R_3P(O)$ compounds is a far better hydrogen bonding agent than that of $(RO)_3P(O)$ compounds. Kosolapoff and McCullough (101) have also shown that hydrogen bonding tendencies decrease in the order $R_2P(O)(OR) > RP(O)(OR)_2 > (RO)_3P(O) > (RO)_2P(O)Cl > (RO)P(O)Cl_2 > P(O)Cl_3$. A similar order was substantiated by the work of Halpern who studied phosphoryl bonding with various polychloro hydrocarbons (102). Therefore, the polarity of the phosphoryl oxygen is directly related to the groups attached to the phosphorus atom and this relationship is exactly the same as was found for the electron availability of the trivalent phosphorus compounds discussed above.

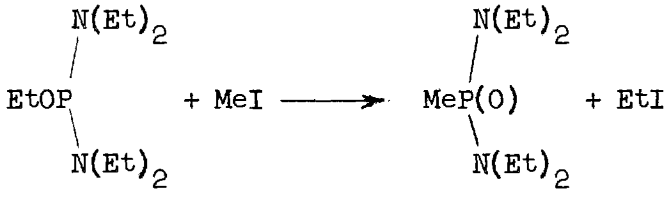
In view of these results, arguments put forth by Dostrovsky and Hallman were analyzed to explain their kinetic data on reactions of phosphorochloridates, $(RO)_2P(O)Cl$, and phosphinyl chlorides, $R_2P(O)Cl$, with various nucleophiles (103). They found that the rate of reaction was proportional to the base strength of the attacking specie (rather than to the nucleophilicity) and that phosphinyl chlorides reacted faster than phosphorochloridates. They attributed the lower rate of reaction of $(RO)_2P(O)Cl$ to the supposition that resonance contributions of the type $R - \overset{\curvearrowright}{\underline{O} -} P \overset{\curvearrowright}{= O}$ would reduce the positive nature of the phosphorus atom as compared to $R - P \overset{\curvearrowright}{= O}$ where such mesomeric effects would be absent. If these arguments are correct, then it is also necessary to predict that the phosphoryl oxygen of $R - \overline{\underline{O}} - P = O$ structures must have a more polar oxygen than in $R - P = O$ structures. Since the exact opposite is true experimentally, there is no choice except to conclude that the suggested mesomeric effects do not occur but that inductive effects predominate. On this basis, the proposed mesomeric explanation is totally inadequate and it is necessary to look elsewhere for the answer. The previously discussed relations between the structure of the phosphorus compound and the hydrogen bonding ability can be advantageously applied here. The phosphoryl oxygen of the phosphinyl compounds can experience a far stronger solvent interaction, thereby leaving the phosphorus atom with more positive charge necessary for faster reaction.

Recent work involving the nuclear magnetic resonance spectra of phosphorus compounds should also be mentioned. An excellent review of the methods and interpretations of this technique has been compiled by Wertz (104). Briefly speaking, this method measures the electron density at the nucleus of the atom itself and can be refined to take into account any perturbation of this density due to other adjacent nuclei, called spin-spin splitting. By making measurements relative to some standard compound, it is possible to obtain a value for a "chemical shift" which is a direct measure of the presence of a greater or smaller electron density around a particular atom as compared to the same atom in the reference compound. In this way, it is possible to measure the effects of substituent groups on the electron shielding of the atom. Negative chemical shift values represent lower electron densities and positive values represent higher electron densities. It is most important to point out that this method is not capable of discriminating among different ways in which electrons can shift, but merely that they shift toward or away from the nucleus.

Gutowsky has applied this technique to the study of fluorine and hydrogen compounds (105) as well as to phosphorus compounds (106). He has pointed out that phosphorus shielding increases on going from $H_2P(O)(OH)$ to $HP(O)(OH)_2$ to $P(O)(OH)_3$, that proton shielding increases on going from $H_2P(O)(OH)$ to $HP(O)(OH)_2$, and that phosphorus shielding is greater in $F_2P(O)(OH)$ than in $P(O)(OH)_3$. He explains the first two of these results as being caused by the importance of $HO^+ = P^-$ type structures and the latter result as being caused by the fact that $F^+ = P^-$ structures are more important than $HO^+ = P^-$ structures. This explanation would also predict that $P(O)F_3$ had a more polar oxygen than $P(O)(OH)_3$, and that F is a better mesomeric constituent than OH. The phosphoryl oxygen in $P(O)F_3$ is not more polar nor could organic chemists agree that F is a better mesomeric constituent than OH. Another explanation of these results is advanced as follows. The inductive nature of the groups on phosphorus determines the position of the phosphoryl electrons. Comparing $H_2P(O)(OH)$ with $HP(O)(OH)_2$, it would then be expected that the added inductive effect would draw the electrons closer to the phosphorus atom thereby increasing both the phosphorus and the proton shielding. Furthermore, substituting (F) for (OH) would draw the electrons even closer and give phosphorus greater shielding than in $P(O)(OH)_3$.

Van Wazer has used the nuclear magnetic resonance method to measure the chemical shifts for phosphorus in many triply- and quadruply-linked compounds (107). He reported large chemical shifts for the trivalent compounds with the shielding generally decreasing with the increasing electronegativity. The odd position of fluorine can be reconciled by perturbation effects since spin-spin splitting is observed in the cases where fluorine substituents are present. The shifts for quadruply connected compounds were much smaller but fell in a consistent order with a negative shift increasing for decreasing electronegativity. Since he used H_3PO_4 for the reference compound, this means that the replacement of oxygen by less electronegative elements gives less shielding. Oxygen to nitrogen shifts were quite constant, indicating that nitrogen substitutes for oxygen the same way each time. A very important point is that this includes substitution of the phosphoryl oxygen with a nitrogen function.

If, as is indicated by Van Wazer, the nitrogen has more <u>pi</u>-bonding than oxygen, then it should be rather stably linked to the phosphorus. That this is not the case is evidenced by several facts. Whereas phosphorus-nitrogen compounds are readily converted to phosphorus-oxygen compounds, the amination of phosphorus-oxygen compounds does not take place (55). In the amination of carboxylic esters to yield amides, one of the important driving forces for the reaction is that in the resulting compound the nitrogen electrons enter into resonance more fully with the carbonyl grouping than did the ester oxygen electrons. Comparison of pK_a changes for aniline versus ammonia and for phenol versus water, and Hammett sigma values indicate that this should be expected. It is difficult to explain then why the phosphoryl linkage, if it does enter into resonance similar to the carbonyl, is not capable of gaining added stability from the nitrogen atoms. Further experimental data are available to indicate that a phosphoryl nitrogen should not be expected to be stable. N-N-dialkyl-O-alkyl-phosphorodiamidites react in a Michealis-Arbusov type reaction to form phosphoryl oxygen product exclusively (108). In this case, the chance for an anion to attack an alkyl substituent was 4:1 in favor of the nitrogen yet the resulting product indicated



$$EtOP(N(Et)_2)_2 + MeI \longrightarrow MeP(O)(N(Et)_2)_2 + EtI$$

that the lone alkyl group on oxygen was attacked. It is, therefore, evident that considerable care must be used in interpreting data regarding phosphoryl nitrogen structures.

The rapid uncatalyzed reaction of phosphorus linked nitrogen groups with formaldehyde, as shown in this thesis work, also indicates that such nitrogens possess more amine than amide character. This amine character is further pointed out in the infrared data of P - N compounds. Primary and secondary amides display a pronounced N - H deformation band in the 1550 cm^{-1} region. While primary amines also exhibit a strong band here, secondary amines display only a very weak band of frequently unmeasurable intensity. The fact that the phosphorus-nitrogen compounds behave like amines rather than like amides in this respect has definitely been established and brings up important questions regarding the interaction of the phosphoryl groupings (109-111). Addison and Sheldon (112) have shown that dinitrogen tetroxide forms molecular compounds with carbonyls through the use of the carbonyl oxygen. Since similar compounds were not formed in the use of sulfonyl or phosphoryl oxygen, they concluded that the oxygen was not bonded in the same manner in all cases. Any attempt to claim pi-bond interaction for phosphorus will also have to explain the known ultraviolet absorption behavior of arylphosphonic acids. Sklar has established that compounds displaying a purely inductive effect, such as $-NH_3^+$, change the spectrum of benzene only slightly and have similar absorption intensities (113). Robertson and Matsen further showed that if the spectrum of a $(Ph)_2X$ compound is very similar to that for (Ph)X, then (X) is a poor resonator (114). The ultraviolet specta of a series of arylphosphonic and arylphosphinic acids have been studied by Jaffe and Freedman and on the basis of the above interpretations they concluded that the phosphoryl linkage had no appreciable pi-bond character (115). Any pi-bond description of phosphorus must also incorporate explanations for the extremely strong nucleophilic character displayed by thiophosphoryl linkages. Whereas $HPO_4^=$ has only mediocre nucleophilic character, $HPO_3S^=$ is the most powerful nucleophile known (57). Its nucleophilic constant is even higher than that of thiosulfate or thiophenolate anion which are generally considered to be very strong reagents. This property suggests that, in the thiophosphoryl linkage, there is a very high concentration of electrons around the sulfur atom, a fact which is not in agreement with pi-bond interaction interpretation.

The lack of activating influence of phosphoryl groupings on alpha halo atoms also suggests a fundamental difference as compared to carbonyl. As described in this thesis (Chapter III), the base-catalyzed reaction which proceeds readily with chloroacetic acid would not proceed with chloromethylphosphonic acid. Similar results using base catalysis with phenol have recently been reported (116).

Attempts to describe the phosphoryl linkage as $P = O$ must also take other evidence into account. Eberhardt has presented molecular orbital picture of the $P(O)X_3$ system using only the s and p orbitals of phosphorus and oxygen (117). He points out that the classical concept of a "double bond" is meaningless in this case since symmetry requires the pi orbitals to appear in pairs. A similar concept has been presented by Chernick and Skinner who favor the use of the structure $R_3\overset{+}{P}\text{-}O^-$ which is modified by back coordination from the $2p_x^{\,2}$ and $2p_y^{\,2}$ orbitals of O^- to the vacant 3d orbitals of P^+ thus giving $P^+ - O^-$ triple bond character (62).

These data indicate that the true nature of the phosphoryl oxygen has not yet been determined. Two important conclusions can be reached, however, which serve as guides toward a better understanding of this intricate problem.

1. Whatever the true nature of the phosphoryl linkage is, it contains a considerable ionic character and this character should be indicated by any symbolism which even attempts to be representative of the actual situation.
2. In view of the highly polar character and in view of the symmetry considerations, the $P = O$ symbolism is both misleading and incorrect.

It is now possible to propose a concept for the nature of phosphoryl compounds which can be used to predict reaction and property changes corresponding to structural modifications. Further, this concept is in agreement with the physical data that are available.

The two main points of this concept deal with:

1. A consideration of the nature of the d orbits of phosphorus. It is proposed that d - d interaction, although of similar type, is of considerably lower magnitude than p - p interaction. It is further proposed that the d orbits are more sensitive to charge changes than p orbits and that under the influence of electronegative substituents, d orbits are altered and approach p orbit type interaction as a limit.
2. The directional properties of d orbits. This directional character taken in conjunction with the bent angular structure of the tetrahedral arrangement demonstrates that if the d orbits are interacting with the phosphoryl atom, it is physically impossible for them to be available for interaction with any other substituent group.

The first characteristic can be used to explain the differences among phosphoryl, thiophosphoryl, and selenophosphoryl linkages. In all cases, the phosphorus atom donates its two electrons to form a bond. In the case of sulfur and selenium, only weak d - d interaction can take place to offset the resulting charges, but in the case of oxygen, stronger p - d interaction takes place. As the charge on phosphorus is modified by added electronegative groups, the d orbit is made more compact and gains more p type character, thus strengthening the interaction and shifting the electron distribution toward phosphorus. In all cases, both the d_{xy} and the

d_{xz} orbits are simultaneously involved. This concept, therefore, neatly explains the observed behavior of oxygen polarity in different structures, the strong nucleophilic character of the thiophosphoryl group, and the nuclear magnetic resonance data.

The directional character of the d_{xy} and d_{xz} orbits pointing toward the phosphoryl oxygen and the fact that the bent tetrahedral structure then places other groups in a position where it is geometrically impossible for interaction to take place (even if the groups have available orbits), accounts for the lack of influence of the phosphoryl group on the benzene spectrum. It further emphasizes that inductive effects should be pronounced since mesomerism cannot occur and explains why the oxygen of an RO - P link is fundamentally different from that of a phosphoryl group.

CHAPTER III

EXPERIMENTAL PROCEDURE

Attempts to Obtain Short Cross-Links in Cellulose

Oxalyl Chloride

Preparation of Oxalyl Chloride.--All attempted perparations using thionyl chloride as the chlorinating agent were not successful. The following is a modification of the method of Staudinger (37), which employed phosphorus pentachloride as the chlorinating agent.

Oxalic acid dihydrate (126 g.) was heated in an oven for five hours at 105° C. to a weight of 90 g., which represented the loss of the water of hydration. To this anhydrous acid, 420 g. of phosphorus pentachloride was added slowly through a powder funnel. The mixture was agitated continuously throughout the addition of the phosphorus pentachloride. During the addition, a slurry began to form and considerable heat was evolved. The reaction was allowed to proceed until a liquid layer formed, and the flask was stoppered and allowed to stand for two days. The flask then was fitted to a fractionating column and a fraction was obtained which had b.p. 61°-63° C. at 760 mm.; m.p. -10° C. Reported (37) for oxalyl chloride: b.p. 63° C. at 763 mm.; m.p. -12° C. A portion of this fraction treated with excess aniline produced a solid product which gave plates from benzene; m.p. 249° C. Reported for oxanilide: plates from benzene; m.p. 249° C.

Reaction of Oxalyl Chloride with Cellulose.--The oxalyl chloride (43 g.) was cooled to 0° C. and was added dropwise to 150 g. of pyridine maintained at 0° C. by cooling in an ice bath. A cellulose sample (15.9 g.) previously dried at 105° C. for five hours was treated in 350 ml. of pyridine. The cellulose sample then was added to the oxalyl chloride-pyridine complex. After reaction at reflux for 18 hours, it was allowed to remain at room temperature for four days. The resulting black mass was diluted with 200 ml. of cold 95 per cent ethanol, filtered, and air-dried.

To determine if any cellulose oxalate had formed, ester interchange with ethyl alcohol was attempted. The treated cellulose was refluxed for three hours in a solution containing 5.0 g. of sodium dissolved in 300 ml. of absolute ethanol. No ethyl oxalate could be detected.

Phosphorus Oxychloride

Reaction of Cellulose with Phosphorus Oxychloride in Pyridine.--Using pyridine as the basic catalyst, 10 g. of cellulose was treated at room temperature in a bath prepared by adding 30 ml. of phosphorus oxychloride to 300 ml. of pyridine. After 10 minutes' immersion, the sample was treated in a two per cent solution of sodium hydroxide, washed in a three per cent acetic acid solution, rinsed, air-dried, conditioned for two days at 65° F. and 70 per cent relative humidity, and tested for strength, viscosity, and phosphorus content. This sample showed no significant difference in its strength as compared to the original sample both by the ravel strip and the IP-2 type tests. The phosphorus content was found to be negligible, and the viscosity in cupriethylene diamine was significantly lower.

Reaction of Soda Cellulose with Phosphorus Oxychloride.--Soda cellulose was prepared by treating cellulose in a 20 per cent solution of sodium hydroxide at room temperature. The sample was padded between paper towels to remove excess solution and dried at 45° C. in a vacuum oven at 30 mm. gauge pressure. The dried sample was treated for 10 minutes at 5° C. in a solution containing 35 g. of phosphorus oxychloride dissolved in 150 ml. of carbon tetrachloride. The cellulose was neutralized in a three per cent acetic acid solution, washed with water, air-dried, conditioned for two days at 65° F. and 70 per cent relative humidity, and tested for strength, viscosity, and phosphorus content. This sample showed a significant loss in strength as compared to the original sample both by the ravel strip and the IP-2 type tests. The phosphorus content was 0.73 per cent and the viscosity in cupriethylene diamine was considerably lowered.

A 10 g. sample of the phosphorylated cellulose was added to a solution of 2.0 g. of sodium sulfide dissolved in 100 ml. of ethylene glycol. The sample was entered at 60° C. and treated for 45 minutes as the liquor cooled. After washing and air drying, the sample was found to have a phosphorus content of 0.097 per cent and to be essentially insoluble in cupriethylene diamine.

Aminomethyl Ethers

Attempted Preparation of Diethylaminomethyl Cellulose Ether.--The reaction of alcohols with formaldehyde and a primary or secondary amine to yield amino ethers and diethers has been reported by Robinson and Robinson (43). To 85 g. of formalin was added dropwise 55 g. of diethylamine, while the mixture was stirred and cooled in an ice bath. To this solution, 5.5 g. of cellulose was added and the whole was treated with 150 g. of anhydrous potassium carbonate. The mass was placed in a mechanical shaker for four hours then allowed to stand for two days, after which the cellulose was washed and dried. Kjeldahl analysis showed a negligible (0.112 per cent) nitrogen content. Heating a duplicate mixture on a water bath for five hours gave similar results.

Attempts to Modity the Anhydroglucose Units

5,6-"Celluloseen"

Preparation of 6-Iodo Cellulose.--A 6.0 g. sample of cellulose was treated for four days at room temperature in a solution containing 70 g. of *para*-toluene sulfonyl chloride (tosyl chloride) dissolved in 117 g. of pyridine (1:10:40 mole ratio of cellulose to tosyl chloride to pyridine). The sample was washed with cold water and air-dried. The sulfur content of the sample was 4.61 per cent which corresponded to approximately one tosyl group for every two anhydroglucose units.

Five grams of this tosylated cellulose was treated in a low-pressure hydrogenation apparatus for six hours at 100° C. with a solution of 50 g. of sodium iodide dissolved in 125 ml. of acetone. After cooling, the sample was removed, washed with water, washed with acetone, and air-dried.

Reaction of 6-Iodo Cellulose with Silver Fluoride.--The silver fluoride was prepared as follows. Silver nitrate (85 g.) was dissolved in water and added to a solution containing 26.6 g. of sodium carbonate. The white precipitate of silver carbonate was filtered and dissolved in 100 ml. of hydrofluoric acid in a platinum dish. The liquid was concentrated with a free flame until considerable crystallization had taken place. After cooling, the resulting black mass was dissolved in water, filtered, and evaporated in darkness in vacuo over concentrated sulfuric acid. Dark brown crystals of the anhydrous salt were obtained.

The 6-iodo cellulose was dried at 105° C. for one hour. A sample of this dry cellulose weighing 2.5 g. was added to a solution of 5.0 g. of anhydrous silver fluoride dissolved in 25 ml. of pyridine. The mass was shaken for 40 hours at room temperature. At the end of this period, the reaction mixture had become a black solution, and the flask covered with a metallic deposit of silver. No cellulosic material could be isolated from the liquor.

Ring Unsaturation

Reaction of Cellulose with Potassium Hydroxide in Chloroform.--A sample of cellulose (4.5 g.) was treated in a 63 per cent solution of potassium hydroxide and was then dried by suction filtration to a weight of 20 g. This cellulose sample was added to 100 ml. of hot chloroform and allowed to reflux for two hours. The sample was removed, neutralized in two per cent acetic acid solution, washed with water, and air-dried. This sample did not discolor bromine solutions in carbon tetrachloride and attempts to determine the bromine content gave negative results.

Reaction of Regenerated Cellulose with Potassium Hydroxide in Chloroform.--A sample of cellulose was dissolved in cupriethylene diamine and was reprecipitated from solution by the addition of sulfuric acid. Twenty grams of cotton linters was precipitated from solution in this manner and was added to a solution of 168 g. of potassium hydroxide dissolved in 175 ml. of water. The liquor was heated to reflux, 50 ml. of chloroform was added, and the solution was maintained at reflux for two hours. The sample was removed, neutralized with two per cent acetic acid, washed with water, and air-dried. Attempts to establish the presence of a double bond gave negative results.

Reaction of Cellulose with Phosphorus Containing Compounds

Phenyl-(N-Phenyl) Phosphonimide

Preparation of Phenyl-(N-Phenyl) Phosphonimide.--To 65.0 g. of aniline hydrochloride (precipitated from ethanol with diethyl ether) was added a slight molar excess (100.0 g.) of phenyldichlorophosphine oxide (this oxide was shown to contain no phenyldichlorophosphine by a negative test with mercuric chloride) dissolved in 25.0 g. of para-xylene. The reaction flask was fitted with a reflux condenser topped with a calcium chloride drying tube. The flask was heated in an oil bath at 120° C. the first day, 150° C. the second day, and 200° C. the third day. During the second day, a complete solution resulted which crystallized into a hard mass on the third day. This solid mass was washed with dry ether to remove any excess phenyldichlorophosphine oxide and any resin products. The product was obtained by dissolving the remaining solid in hot alcohol-free chloroform and reprecipitating from the cooled liquor with anhydrous ether. The product was further purified by recrystallization from hot thiophene-free benzene previously distilled from phosphorus pentoxide and stored over sodium. Found m.p. 297° C.; reported m.p. 290° C. (56).

Anal. Calc. for $C_{12}H_{10}NPO$: P, 14.50; Found: P, 14.40.

Reaction of Phenyl-(N-Phenyl) Phosphonimide with Cellulose.--Cellulose was dried in an oven at 105° C. for one hour. Five grams of this dried cellulose was placed in a solution containing 10.0 g. of phenyl-(N-phenyl) phosphonimide dissolved in 100 ml. of chloroform, the flask was fitted with a reflux condenser capped with a calcium chloride drying tube, and the reaction refluxed for five hours. After cooling, the cellulose was washed several times with hot chloroform and conditioned in air. Analysis showed the phosphorus content to be negligible.

Halomethylphosphonic Acid and its Derivatives

Preparation of Iodomethyldiethylphosphonate.--This compound could be prepared by a procedure described by Ford-Moore (59) but was prepared more satisfactorily by the method of Arbusov and Kuskova (58) as follows. Methylene iodide (24.0 g.) was added to triethyl phosphite (15.0 g.) and the flask was fitted with a reflux condenser. The liquor was heated to 110° C., at which point a vigorous exothermic reaction ensued. After the reaction subsided, the flask was allowed to stand overnight and the liquor was fractionated to give 5.11 g. of product; b.p. 108° C. at 1.2-1.5 mm.; n_D^{17} 1.4970. Reported (58) b.p. 133° C. at 6 mm., 101° C. at 0.7 mm.; calc., 108° C. at 1.2 mm.; n_D^{17} 1.4975.

Reaction of Cellulose with Iodomethyldiethylphosphonate.

Method 1.--A cellulose sample (0.50 g.) was soaked in a 15 per cent sodium hydroxide solution, padded dry between paper towels, and then soaked in 2.0 g. of iodomethyldiethylphosphonate. This sample was heated in an oven for 30 minutes and was washed, neutralized in five per cent acetic acid, washed, and then rinsed several times in hot acetone to remove any excess phosphonate.

Method 2.--Another experiment was performed in exactly the same manner except that the cellulose, after being treated with the concentrated caustic, was washed in acetone to remove the water before being treated with the iodomethyldiethylphosphonate.

Method 3.--A sample of cellulose (0.50 g.) was treated in a 15 per cent sodium hydroxide solution, padded dry, and then passed through several acetone baths to remove excess water. This sample was placed in a solution containing 2.0 g. of iodomethyldiethylphosphonate dissolved in 60 ml. of acetone and refluxed for three days, after which it was washed and neutralized in the above described manner.

Method 4.--A sample of cellulose weighing 0.50 g. was treated with a solution conatining 2.0 g. of iodomethyldiethylphosphonate dissolved in 3.0 g. of pyridine. The sample was then baked in an oven at 100° C. for one hour, after which it was washed and dried.

The products isolated from each of these reactions were conditioned in air for at least 24 hours. Analysis showed that each had a negligible phosphorus content.

Reaction of Cellulose with Chloromethyldipropylphosphonate.--Chloromethyldipropylphosphonate (10.0 g.) supplied by the Victor Chemical Company was dissolved in 10.0 g. of pyridine. A 1.0 g. sample of cellulose was treated with this solution for 48 hours at room temperature. The sample was then pressed to remove most of the pyridine solution and heated in an oven at 100° C. for one hour. It was washed with water and then with acetone to remove any excess phosphonate. Analysis of the sample after conditioning in air showed the phosphorus content to be negligible.

Reaction of Cellulose with Chloromethylphosphonic Acid.

Method 1.--A cellulose sample (2.0 g.) was treated for 30 minutes at room temperature in a solution containing 10.0 g. of water and 20.0 g. of chloromethylphosphonic acid (supplied by the Victor Chemical Company). The sample was padded to a weight of 3.86 g. and was dispersed into a 40 per cent solution of sodium hydroxide. After 30 minutes, the sample was removed from the sodium hydroxide and one-half of it was heated in an oven at 110° C. for 45 minutes. Both samples were neutralized in a two per cent alcoholic acetic acid solution, rinsed with pure alcohol, dried, and conditioned in air.

Method 2.--In a second similar procedure, the chloromethylphosphonic acid was first converted to its disodium salt before being applied to the cellulose. The sample was then treated in the manner described above.

Method 3.--The use of pyridine as the basic catalyst was also attempted. A 2.0 g. sample of cellulose was treated in a solution containing 10.0 g. of chloromethylphosphonic acid dissolved in 25.0 g. of pyridine. The treated sample was then heated in an oven at 100° C. for one hour, after which it was neutralized, washed with alcohol, and conditioned in air.

Analysis of each of these three products revealed that its phosphorus content was negligible.

Phosphites

Reaction of Cellulose with Triphenyl Phosphite.

Method 1.--A 2.0 g. sample of cellulose was placed in a 500 ml. side armed flask and was covered with 100 ml. of triphenyl phosphite. The flask was heated for six hours at 240° C. and some charring of the cellulose occurred at this high temperature. After cooling, the sample was washed in hot methanol to remove any impurities and unreacted starting compound. Analysis showed that the phosphorus content of the sample was negligible.

Method 2.--This procedure employed pyridine catalyst. A 2.0 g. sample of cellulose was placed in a flask containing 15.0 g. of pyridine dissolved in 100 g. of triphenyl phosphite, and the liquor was heated at

115° C. for 12 hours. After cooling, the sample was removed and washed with hot methanol to dissolve excess phosphite. Analysis showed that the sample had a negligible phosphorus content.

Method 3.--The above-mentioned results are in contrast to those obtained using sodium hydroxide as catalyst. A 2.0 g. sample of cellulose was treated in a 20 per cent sodium hydroxide solution for five minutes at room temperature and excess base then was removed by padding. This sample was placed in a flask containing 75 ml. of triphenyl phosphite and was heated at 55° C. for six hours. The sample was cooled and washed several times in hot ethanol to remove excess phosphite. Analysis showed that the sample contained 8.58 per cent phosphorus.

Method 4.--In a further extension of this work, diluted solutions of triphenyl phosphite were tried to determine if smaller percentages of phosphorus could be introduced. A 1.0 g. sample of cellulose was treated for five minutes at room temperature in a 20 per cent sodium hydroxide solution. The sample was then padded dry and placed in a solution containing 30 ml. of triphenyl phosphite dissolved in 50 ml. of carbon tetrachloride. The reaction was refluxed for 48 hours after which the sample was removed and washed in hot methanol to remove any unreacted phosphite. The sample thus prepared gave no analysis for phosphorus.

Reactions of Phosphited Cellulose.

Hydrolysis.--The cellulose sample that had acquired rather unique properties by reaction with triphenyl phosphite retained its translucency and gelatinuous texture even under some drastic hydrolytic conditions. Phosphited samples (0.50 g.) prepared as above showed no apparent change after boiling for 30 minutes in either 100 ml. of 20 per cent (by volume) acetic acid solutions or 100 ml. of eight per cent (by weight) potassium carbonate solutions. Boiling a 0.50 g. sample of phosphited cellulose for 30 minutes in 100 ml. of water containing 15 per cent sodium hydroxide (based on the weight of the sample) decreased the phosphorus content from 4.98 per cent to 2.77 per cent and caused a corresponding decrease in the gelatinous texture of the cellulose.

Aging.--Upon standing in the atmosphere for extended periods of time, the phosphited cellulose samples lost their property of becoming translucent and gelatinous on treatment with water, even though they retained their phosphorus content. To determine if a change in the oxidation state of phosphorus could be responsible for this behavior, several reactions were attempted which are known to alter trivalent phosphorus compounds. A 0.50 g. sample of freshly prepared phosphited cellulose was boiled for 30 minutes in 100 ml. of 10 per cent (by volume) hydrogen peroxide. This treatment had no apparent effect on the properties of the cellulose. Brown alcoholic iodine solutions are rapidly decolorized by triphenyl phosphite at room temperature. A 100 ml. portion of an alcohol iodine solution, of such strength as to be completely decolorized by one drop of triphenyl phosphite at room temperature, was not decolorized by 30 minutes boiling with a 1.0 g. sample of the phosphited cellulose. Similarly, a suspension of sulfur in carbon tetrachloride, capable of being completely cleared at room temperature by one drop of triphenyl phosphite, did not undergo any change when boiled for 30 minutes with a 1.0 g. sample of phosphited cellulose.

Reaction of Cellulose with Triethyl Phosphite.--A 1.0 g. sample of cellulose was treated for five minutes at room temperature in a 20 per cent sodium hydroxide solution and then was padded dry. This sample was placed in a 50 ml. thermowell flask containing 30 ml. of triethyl phosphite. The temperature slowly rose from 25° to a maximum of 44° C. and remained there for 30 minutes before starting to decline. The flask was stoppered and allowed to stand overnight. The reaction was then heated at 80° C. for three hours. A white solid substance began to appear in quantity throughout the phosphite liquor as the temperature was raised. After cooling, the cellulose was washed in warm acetone and then in water. Analysis showed that the sample contained 1.27 per cent phosphorus.

Reaction of Cellulose with Triallyl Phosphite.--A 1.9 g. sample of cellulose was treated for five minutes at room temperature in a 20 per cent sodium hydroxide solution and was padded dry. This sample was placed into a flask containing 50 ml. of triallyl phosphite. The sample was heated to 90° C. over a 10-minute period and remained in the cooling liquor for one hour. The sample was washed several times in warm acetone and dried. Phosphorus analysis showed that the sample contained no phosphorus.

Reaction of Cellulose with Dimethyl Hydrogen Phosphite.

Base-Catalyzed Reaction.--A 1.0 g. sample of cellulose was treated in a 20 per cent sodium hydroxide solution for five minutes at room temperature and then was padded to a weight of 2.0 g. This sample was then placed in a 50 ml. thermowell flask containing 25 ml. of dimethyl hydrogen phosphite. The temperature immediately rose from 25° to 40° C. and then slowly declined. The reaction was then heated at 77° C. for 17 hours. The sample was removed and washed several times in warm acetone and then in water. Analysis showed that the sample contained 1.90 per cent phosphorus.

Todd-Type Reaction.--Dimethyl hydrogen phosphite (22.0 g.) was dissolved in 40 ml. of chloroform containing 15.8 g. of pyridine. A sample of cellulose weighing 2.0 g. was added and the reaction was heated at reflux for four hours. The liquor soon began to turn yellow, a reddish oil then appeared at the surface of the liquor, and finally the cellulose gained a reddish appearance. On removal of the sample, it was noted that the cellulose was covered with a very viscous reddish substance that was extremely soluble in cold alcohol. The sample was washed several times in hot methanol but still retained a slight orange coloration. Analysis showed that the sample contained 1.78 per cent phosphorus.

Reaction of Phenyldiamidophosphoramidates with Formaldehyde

Phenyldiamidophosphoramidate

Preparation of Phenyldiamidophosphoramidate.--This material was prepared using the method described by Audrieth and Toy (70) which employs a 1:0.77:3 mole ratio of phosphorus oxychloride to phenol to pyridine. A solution of 94 g. of phenol (U.S.P. crystals) dissolved in 237 g. of pyridine was added in a dropwise manner to a solution containing 199 g. of phosphorus oxychloride dissolved in 500 ml. of chloroform. The reaction was stirred and maintained at -2° ± 2° C. throughout the addition. This mixture was then added dropwise with stirring to a flask containing 300 ml. of liquid ammonia. The flask containing the liquid ammonia was surrounded by a dry ice-acetone bath and fitted with both a ground glass stirrer and a large capacity cold finger filled with dry ice-acetone. After the addition was complete, the reaction was stirred for 15 minutes longer, and then the excess ammonia was allowed to evaporate. The remaining solid was filtered, dried, and washed free of excess ammonium chloride with cold water. The remaining waxy solid was air-dried and recrystallized several times from hot 95 per cent alcohol to give plates; m.p. 183° C.; 30 per cent yield; reported: m.p. 183°-184°C.

By using a modification of the above procedure, it was possible to obtain better yields of a purer product. Instead of using 300 ml. of liquid ammonia, it is possible to beneficially utilize saturated ammonia water. This saturated liquor was prepared by taking 750 ml. of concentrated ammonium hydroxide, cooling it in a dry ice-acetone bath and bubbling in ammonia gas until the volume had increased about 150 ml. The chloroform liquor was then added in a dropwise manner to this liquor and, after addition was complete, the chloroform layer was separated rapidly and filtered to give a product that was essentially free from the ammonium chloride impurity. The advantage to this procedure was further pointed out in that it was necessary to use only 2.5 liters of hot 95 per cent alcohol to dissolve 100 g. of crude product as compared to six liters needed to dissolve a similar weight of product obtained by the use of liquid ammonia. The yields in this case were of the order of 60 per cent.

Reaction of Phenyldiamidophosphoramidate with Paraformaldehyde and Pyridine Hydrochloride.--The phenyldiamidophosphoramidate (8.6 g.; 0.05 mole) was added to a dispersion of 3.0 g (0.10 mole) of paraformaldehyde in 75 ml. of pyridine. The mixture was stirred and heated at 75° C. for one hour and, at the end of that time, all of the solid had reacted giving a product which was completely soluble in the pyridine. The solution then was cooled to room temperature and 11.5 g. of pyridine hydrochloride was added. The hydrochloride dissolved rapidly at room temperature. The reaction was then heated for two hours at 75° C. and, if the agitation was discontinued, relatively large amounts of a yellowish oil settled to the bottom of the flask.

If the reaction was continued at 75° C. for 14 hours longer, the oil was converted to a white granular solid. After filtering and air-drying this solid weighed 5.9 g. and was extremely soluble in cold water but was insoluble in hot carbon tetrachloride, absolute ethanol, dioxane, nitrobenzene, ethyl acetate, ether, acetone, chloroform, dimethyl formamide, nitromethane or acetonitrile. It was purified by dissolving in the minimum amount of cold water and then reprecipitating by the addition of a large amount of acetone.

Found: N, 23.7; Cl, 26.9; P, none.

Evaporation of the liquid layer from which the solid separated yielded a clear adhesive liquid of high viscosity. When this liquid was spread on a watch glass and heated in an oven, it yielded tough clear films. Another experiment using chloroform as the solvent and employing only molar quantities of pyridine gave essentially the same results.

Reaction of Phenyldiamidophosphoramidate with Paraformaldehyde in Chloroform.--To 50 ml. of chloroform was added 8.6 g. (0.05 mole) of phenyldiamidophosphoramidate and 3.0 g (0.10 mole) of paraformaldehyde. This mixture was stirred and heated at reflux for three hours to yield a clear solution. This solution on evaporation did not yield any solid but produced a viscous tacky oil. If some of the original solution was poured on a watch glass and heated in an oven at 100° C. for one hour, a clear tightly adhering film was produced.

A second reaction conducted in exactly the same manner, except that heating was continued over a 64 hour instead of a three hour period, produced a modification of the film forming product. Evaporation of this liquor yielded a wax-like product instead of a tough film.

Reaction of Phenyldiamidophosphoramidate with Formalin.--Phenyldiamidophosphoramidate (1.73 g.; 0.01 mole) was added to 1.62 g. (0.02 mole) of 37 per cent formalin which had been diluted with 5 ml. of water. This mixture was shaken for 8 hours at room temperature and then allowed to stand for an additional 16 hours. Most of the solid phosphoramidate still remained at the end of this time, and an 85 per cent recovery of the starting phosphoramidate was obtained. As a comparison, 1.73 g. of phenyldiamidophosphoramidate was added to a small flask containing 6 ml. of water only. This flask was also shaken for 8 hours at room temperature and then was allowed to stand for an additional 40 hours. It was possible to recover 98 per cent of the starting compound in this case.

If the reaction was heated, a different result was obtained. Phenyldiamidophosphoramidate (8.6 g.; 0.05 mole) was added to 8.1 g. of 37 per cent aqueous formaldehyde (0.10 mole) dissolved in 30 ml. of water. The reaction was stirred and heated to reflux over a 15-minute period and gave a clear solution. Heating was then discontinued and the flask was allowed to cool. On cooling the solution became cloudy and, on standing overnight, a viscous clear syrupy mass settled to the bottom of the flask. The water was decanted and the flask was rinsed with 20 ml. of cold acetone to remove any remaining water. The syrup was very soluble in cold chloroform and upon evaporation, clear films resembling those obtained from the previously described reactions resulted.

Diphenylmonoamidophosphoramidate

Preparation of Diphenylmonoamidophosphoramidate.--This compound is readily available, since it is produced as a side reaction product in the preparation of phenyldiamidophosphoramidate. The diphenylmonoamidophosphoramidate is very soluble in chloroform, and evaporation of the chloroform layer obtained from the preparation of phenyldiamidophosphoramidate by the liquid ammonia procedure yields small amounts of the diphenyl compound. The diphenylmonoamidophosphoramidate produced yielded needle-shaped crystals on recrystallization from chloroform which melted at 146°-147° C. The reported value for the compound lists needles from chloroform which melt at 146° C.

Reaction of Diphenylmonoamidophosphoramidate with Paraformaldehyde in Chloroform.--To 1.25 g. (0.005 mole) of diphenylmonoamidophosphoramidate was added 0.30 g. (0.01 mole) of paraformaldehyde and 30 ml. of chloroform. The reaction was stirred and refluxed for three hours and gave a clear solution. This solution on evaporation of the chloroform produced a less tacky oil than that produced by the monophenyl compound. This solution on standing for extended periods did not produce any type of solid residue as had been the case with the monophenyl compound.

Phenyldi(methylamido)phosphoramidate

Preparation of Phenyldi(methylamido)phosphoramidate.--A solution of 47 g. of phenol (U.S.P. crystals) dissolved in 119 g. of pyridine was added in a dropwise manner to a solution containing 99.5 g. of phosphorus oxychloride dissolved in 300 ml. of chloroform. The reaction was stirred and maintained at -2° ± 2° C. during the addition. This solution was then added in a dropwise manner to 500 ml. of 25 per cent aqueous methylamine solution which was maintained at -5° C. The chloroform layer was separated and evaporated under reduced pressure with slight heating to yield 68 g. of a light yellow crude product. This product lost considerable weight on being washed with water. The remaining solid was then recrystallized from hot carbon tetrachloride to give 23 g. of product that melted at 103° C. The reported value for this compound lists crystals from carbon tetrachloride of melting point 103° C.

Reaction of Phenyldi(methylamido)phosphoramidate with Paraformaldehyde in Chloroform.--To a solution of 4.00 g. (0.02 mole) of phenyldi(methylamido)phosphoramidate dissolved in 50 ml. of chloroform was added 1.2 g. (0.04 mole) of paraformaldehyde, and the reaction was stirred and heated to reflux. After 30 minutes, the solid went into complete solution and the reaction was then further heated for 4 hours more. All attempts to obtain a pure product by the evaporation of the solvent resulted in the production of a film-forming material similar to that previously described for the diamido compound. Heating the reaction for 48 hours at reflux or allowing the resulting chloroform solution to stand for extended periods of time did not result in the production of any precipitated solid.

Reaction of Phenyldi(methlyamido)phosphoramidate with Formalin.--A 2.0 g. sample of the phenyldi(methylamido)phosphoramidate was added to 1.62 g. of 37 per cent aqueous formaldehyde which had been diluted with 5 ml. of water. After 15 minutes of shaking at room temperature, all of the solid went into solution. This solution was allowed to air evaporate overnight and yielded a very viscous clear syrup which did not smell of formaldehyde. This syrup turned methyl orange red and was soluble in acetone, *t*-butyl alcohol, dioxane, and ethyl acetate but was insoluble in benzene. All attempts to obtain crystals from solutions in cellosolve, dimethyl formamide, dioxane, butyl acetate, diethyl ketone, acetone, chloroform, and absolute ethanol were unsuccessful. Analysis showed that the syrup had a 12.9 per cent phosphorus content.

A second 2.0 g. sample of phenyldi(methylamido)phosphoramidate was added to 6 ml. of plain water to note any hydrolysis effects. After standing at room temperature for two days, 98 per cent of the starting compound was recovered from the sample.

Phenyldianilidophosphoramidate

Preparation of Phenyldianilidophosphoramidate.--A solution containing 47 g. of phenol (U.S.P. crystals) dissolved in 119 g. of pyridine was added dropwise to a solution containing 99.5 g. of phosphorus oxychloride dissolved in 250 ml. of chloroform. The reaction was stirred and maintained at -2° ± 2° C. during the addition. This solution was then added in a dropwise manner to 372 g. (4.0 moles) of aniline at 4° C. The liquor was then filtered free of aniline hydrochloride salt and allowed to air evaporate overnight to remove excess chloroform. The liquor was then heated on a water bath to remove excess pyridine and the solid obtained on cooling was recrystallized four times from hot 80 per cent alcohol giving 70 g. of a fluffy bluish-white solid that melted at 178° C.-179° C. The reported value lists the melting point as 179° C.

Reaction of Phenyldianilidophosphoramidate with Paraformaldehyde in Chloroform.--The phenyldianilidophosphoramidate (3.25 g; 0.01 mole) was added to 0.60 g. (0.02 mole) of paraformaldehyde dispersed in 60 ml. of chloroform, and the reaction was stirred and refluxed for 14 hours. After cooling, 1.8 g. of unreacted solid phosphoramidate was isolated and upon evaporation of the chloroform 1.4 g. of this starting compound was yielded; or a total recovery of 99 per cent of unreacted compound.

Reaction of Phenyldianilidophosphoramidate with Formalin.--Aqueous 37 per cent formaldehyde (1.63 g.) was stirred and refluxed for 24 hours with

3.25 g. of phenyldianilidophosphoramidate in 50 ml. of water. The solid remained essentially unreacted since it was possible to recover 3.2 g. or 99 per cent of the starting phosphoramidate.

Reaction of Phenyldianilidophosphoramidate with Paraformaldehyde in Absolute Ethanol.--Phenyldianilidophosphoramidate was reacted with paraformaldehyde in a 1:2 mole ratio using absolute ethanol as the solvent. The reaction was stirred and refluxed for 24 hours and, on cooling and evaporating the solvent, it was possible to recover 98 per cent of the starting phosphoramidate compound.

Reactions of Phenyldiamidophosphonamidates with Carbonyls

Phenyldiamidophosphonamidate

Preparation of Phenyldiamidophosphonamidate.--This compound was prepared according to a procedure outlined by Michealis (72), which utilizes phenyldichlorophosphine oxide and ammonia. The phenyldichlorophosphine oxide was Eastman yellow label reagent and was used without further purification. To a two-liter flask fitted with a large cold finger and a ground-glass stirrer was added 500 ml. of chloroform. The flask was cooled in, and the cold finger filled with, dry ice-acetone mixture and then 200 ml. of liquid ammonia was added. The liquid ammonia-chloroform was stirred while 125 g. of phenyldichlorophosphine oxide was added in a dropwise manner. After the addition was complete, the cooling mixture was removed and the excess ammonia was allowed to evaporate. The solid was then filtered, washed with cold water to remove ammonium chloride, dried by air evaporation, and recrystallized from hot 95 per cent ethanol. It was necessary to use as much as four liters of hot ethanol to dissolve 70 g. of this crude product. A final yield of 36 per cent was obtained after two recrystallizations.

Using the same procedure but employing n-hexane as the solvent, it was possible to get only 25 per cent yields. By using cold saturated ammonia solutions of ethanol or water, a purer product could be obtained as evidenced by the fact that far less ethanol was required for recrystallization purposes. Since water can dissolve 89.9 g. of ammonia at 0° C., 300 ml. of concentrated ammonium hydroxide (27 per cent) was placed in a liter flask surrounded by an ice bath, while the temperature was maintained at 0° C. and a brisk stream of ammonia was bubbled through for 30 minutes. A total of 50 g. of phenyldichlorophosphine oxide was then added dropwise. After completion of the addition, the mass was quickly filtered and washed with excess cold water to remove any ammonium chloride that may not have dissolved in the water layer of the reacting liquor. After air-drying, the solid was recrystallized from 200 ml. of hot ethanol to give 37.5 per cent yields of a product melting sharply at 188° C. The reported value lists 188° C. as the melting point. Ammoniacal alcohol solutions also gave similar results.

Reaction of Phenyldiamidophosphonamidate with Formalin.--Several sets of conditions were employed for this reaction and they will be described below.

Reaction in a 1:2 Mole Ratio.--To 20 ml. of water in a small flask was added 8.15 g. (0.10 mole) of 37 per cent formaldehyde and 7.8 g. (0.05 mole) of phenyldiamidophosphonamidate and the mixture was agitated manually. In approximately five minutes' time, the temperature of the solution rose from 25° to 58° C. and all of the solid had gone into solution. The resulting solution was allowed to come to room temperature, filtered, and air-evaporated to give shiny plates which were then washed with absolute alcohol to remove any adhering water. These plates were recrystallized from hot 95 per cent alcohol to give plates melting sharply at 226°-227° C.

Reaction in a 1:1 Mole Ratio.--To 20 ml. of water in a small flask was added 4.08 g. (0.05 mole) of 37 per cent formaldehyde and 7.8 g. (0.05 mole) of phenyldiamidophosphonamidate and the mixture was shaken. Considerable heat was evolved, but, after the heating had stopped, there still remained a farily large amount of solid. This solid was filtered, washed clean with excess water and air-dried to give a weight of 2.2 g. which melted sharply at 188° C. and did not depress the melting point of an authentic sample of the starting phosphonamidate. The liquor on air evaporation yielded a product which did not give a sharp melting point even after five recrystallizations from alcoholic solution.

Reaction with Water Only.--To determine if hydrolysis due to the action of water alone was taking place, the above-mentioned experiments were repeated with the formaldehyde omitted. The mixture was mechanically agitated for two hours and then allowed to stand at room temperature for five days. The solid, recovered in 98 per cent yield, was shown to be starting compound.

Reaction in a 1:2 Mole Ratio at Controlled Heat.--Since the above-mentioned experiment demonstrated that water by itself at 30° C. was not capable of hydrolyzing the phosphonamidate, it was necessary to determine if the reaction with aqueous formaldehyde would proceed with any reasonable speed at this temperature or if simple hydrolysis from the heated water solvent was the factor accounting for the previous reaction. To 5.0 ml. of water in a small flask was added 16.2 g. (0.20 mole) of 37 per cent formaldehyde and 15.6 g. (0.10 mole) of phenyldiamidophosphonamidate. The flask was shaken and the temperature was maintained at 30° C. by the use of an ice bath. The time for the total solids to go into complete solution at this temperature was 30 minutes. The solution was then filtered and air-evaporated to give plates which were recrystallized several times from hot 95 per cent alcohol and yielded plates of melting point 226°-227° C.

Anal. Calc. for $C_6H_{10}NPO_3$: C, 41.17; H, 5.72; N, 8.00;
P, 17.70

Found: C, 41.90; H, 5.82; N, 7.99; P, 17.42

Synthesis of Phenylmonoammoniumphosphonic Acid.--To 18.0 ml. of water in a small beaker was added 1.58 g. (0.01 mole) of phenylphosphonic acid (research sample obtained from Victor Chemical Company) and 0.6 g. of 27 per cent ammonium hydroxide. This solution was air-evaporated and the solid was then treated with a warm 50-ml. portion of absolute alcohol to dissolve any free phenylphosphonic acid which is readily soluble in this reagent. The remaining solid was recrystallized from hot 95 per cent ethanol and produced plates having a melting point of 226°-227° C. An infrared curve was run on this compound by the potassium bromide pellet technique and was identical with an infrared curve run on the compound described above.

Reaction of Phenyldiamidophosphonamidate with Paraformaldehyde in Chloroform.--Phenyldiamidophosphonamidate (7.8 g.; 0.05 mole) and paraformaldehyde (3.0 g.; 0.10 mole) were dispersed in 60 ml. of chloroform and the mixture was then stirred and heated at reflux for 24 hours. The flask was cooled and a white solid was separated. The solid was allowed to air-dry and was found to be extremely soluble in cold water. This was interesting since neither of the starting materials possessed any degree of water solubility. The solid was recrystallized by extracting with successive 200-ml. portions of hot 95 per cent ethanol. The first extract dissolved one product which was evidently readily soluble and, from the other alcoholic portion, it was possible to obtain long, clear, needle-shaped crystals which melted sharply at 240°-241° C. An infrared spectrum was made on this product using the potassium bromide pellet technique.

Anal. Calc. for $C_{12}H_{18}N_2P_2O_5$: C, 43.38; H, 5.46; N, 8.43;
P, 18.64

Found: C, 43.78; H, 5.63; N, 8.69; P, 18.30

Preparation of the Silver Salt.--One gram of the above-mentioned reaction product was dissolved in 10 ml. of water and to this solution was added 20 ml. of five per cent silver nitrate solution. A white precipitate was immediately formed which was filtered and washed with 20 ml. of cold water to remove excess silver nitrate. This solid was air-dried overnight to a weight of 1.2 g. Upon being tested for its nitrogen content by the Kjeldahl method, the solid was found to contain 0.02 per cent nitrogen. An infrared spectrum made on the powder using the potassium bromide pellet technique was found to be identical with the infrared spectrum of the original compound except for the absence of some strong bands which had previously been assigned as ammonium bands.

Acid Hydrolysis.--An 0.50 g. sample of the paraformaldehyde reaction product was dissolved in 20 ml. of cold water and 20 ml. of concentrated hydrochloric acid was added. A precipitate was formed immediately, which was interesting since pure phenylphosphonic acid under identical conditions does not yield a precipitate. The precipitate was filtered and air-dried overnight. A nitrogen analysis on this precipitate showed an 0.04 per cent nitrogen content. If the precipitate was melted starting at room temperature, it appeared to sinter and finally melted at 205° C. If the melting point tube first was placed in the heating block at temperatures around

123° C., the solid melted immediately and then resolidified on further heating; finally melting again at 205° C.

If the above experiment was repeated and the precipitate was not removed but was allowed to remain in contact with the acid solution at 25° C. for two days, it redissolved. This solution on air evaporation gave plates which melted sharply at 158°-159° C. and were found not to depress the melting point of an authentic sample of pure phenylphosphonic acid.

Attempted Synthesis of Phenyldiammoniumpyrophosphonic Acid.--Several attempts were made to prepare this compound separately in order to substantiate further the structure of the reaction product of phenyldiamidophosphonamidate with paraformaldehyde in chloroform.

Controlled Low-Temperature Hydrolysis.--To 45 ml. of chloroform was added 5.4 g. (0.3 mole) of water and the dispersion was vigorously stirred while 39 g. (0.20 mole) of phenyldichlorophosphine oxide was added slowly. Until approximately three-fourths of the dichloro compound had been added, the liquid became a cloudy white and essentially no reaction occurred. The solution then became quite warm and cleared completely and the reaction was accompanied by copious evolution of hydrogen chloride gas. The rest of the phenyldichlorophosphine oxide was then added and the solution was heated at reflux for four hours. After two hours, the fairly pronounced evolution of hydrogen chloride subsided and a white solid appeared in the flask. To insure complete removal of the hydrogen chloride, the solution was placed under reduced pressure every 15 minutes for the remaining two hours. The white solid was filtered off, washed with clean chloroform and air-dried to give 11.0 g. of a white powdery solid. The chloroform solution on evaporation yielded 14.0 of a white solid. Both products melted at 158° C. and neither depressed the melting point of an authentic sample of pure phenylphosphonic acid.

Controlled High-Temperature Hydrolysis.--Since the above experiment may have failed to give the desired product because of insufficient heating due to the limited boiling point of the solvent employed, the reaction was repeated without the use of solvent. To 39 g. (0.20 mole) of phenyldichlorophosphine oxide was added dropwise 5.4 g. (0.30 mole) of water. The main liquor was subjected to continuous vigorous sitrring throughout the whole period of addition and also throughout the whole reaction period. After 3.0 g. of water had been added, the mixture warmed considerably and copious amounts of hydrogen chloride were evolved. Addition of water was continued during this period. The reaction then slowly subsided, evolution of hydrogen chloride practically ceased, and a thick syrupy clear solution resulted. This solution was heated to 200° C. over a period of one hour and then kept at 200°-205° C. for six hours. Heat was then removed and on cooling the liquid solidified to a hard transparent mass. The solid mass was refluxed for three hours with 300 ml. of benzene that had been distilled over phosphorus pentoxide and stored over sodium ribbon. The yellowish benzene layer was then separated and on cooling gave a white powder. This product did not redissolve in more hot benzene when it was heated with more benzene in an attempt to recrystallize it to a purer state. The white solid was air-dried, melted at 158° C. and did not depress the melting point of an authentic sample of pure phenylphosphonic acid.

Reaction of Urea with Phenylphosphonic Acid.--Davis (30) has reported that he was able to prepare diammonium pyrophosphate by heating phosphoric acid with an excess of urea at 175° C. An attempt was made to determine if phenylphosphonic acid would behave in a similar manner. Phenylphosphonic acid (15.8 g.; 0.10 mole) was mixed with an excess (10.0 g.) of urea, and the mixture was heated at 175° C. for 12 hours and then was heated at 195° C. for 4 hours longer. All attempts to isolate a pyrophosphate from this reaction yielded only one product that was shown to be phenylphosphonic acid.

Dehydration.--According to Michealis (74) a glassy state solid can be obtained by heating phenylphosphonic acid at 200°-205° C. until the weight loss corresponds to the loss of one water molecule for every two molecules of the phenylphosphonic acid. If heating is continued until the weight loss corresponds to the loss of two water molecules for every three molecules of the phenylphosphonic acid, Michealis proposed that the product represented a polyphosphate. A sample of phenylphosphonic acid was dried at 148°-150° C. for one hour. A portion of this dried sample weighing 17.9560 g. was then heated at 200° C. until it lost 1.0790 g. which corresponded to a 6 per cent loss in weight. The theoretically predicted value called for a 5.69 per cent weight loss.

One-half of the sample thus prepared was dissolved in 125 ml. of cold dioxane which had been purified and stored over sodium ribbon. This solution was then diluted 1:1 with anhydrous ether and cooled until the dioxane began to crystallize. In a separate flask 40 ml. of dry ether was cooled and saturated with ammonia gas. This saturated ammonia solution was then added to the solution of phenylphosphonic acid dehydration product until a faint smell of ammonia could be detected. The precipitate so obtained was filtered and washed with cold anhydrous ether and stored over phosphorus pentoxide in a dessicator. This solid was recrystallized from hot 95 per cent alcohol and gave plates that melted at 226°-227° C. and had an infrated spectrum that was identical with the spectrum for phenylmonoammoniumphosphonic acid.

Reaction of Phenyldiamidophosphonamidate with Paraformaldehyde in Carbon Tetrachloride.--To 7.8 g. of phenyldiamidophosphonamidate dispersed in 60 ml. of carbon tetrachloride was added 3.0 g. of paraformaldehyde and the mass was stirred and heated at reflux. After 30 minutes, the suspension began to agglomerate and stick to the sides of the flask. This solid which appeared to be composed of plates of the starting phosphonamidate that had a sticky surface because of some partial reaction was scraped off the sides of the flask and the heating and stirring continued for 24 hours. A solid white powder was obtained which was water-soluble and could be recrystallized from hot 95 per cent alcohol to give clear needles melting at 240°-241° C. An infrared spectrum on these needles showed that they were identical with the product of the same reaction using chloroform as the solvent.

Reaction of Phenyldiamidophosphonamidate with Benzaldehyde in Chloroform.--To 60 ml. of chloroform was added 7.8 g. (0.05 mole) of phenyldiamidophosphonamidate and 10.6 g. (0.10 mole) of benzaldehyde. The mixture was stirred and brought to reflux. After refluxing for 24 hours, the reaction was cooled and the white solid was separated, washed with several portions of chloroform to remove any occluded benzaldehyde, and air-dried to give 7.6 g. of an extremely water-soluble product. This solid was dissolved by treating with two successive 100-ml. portions of hot 95 per cent alcohol. On cooling, the first portion produced plate-shaped crystals having a rather poorly defined melting point in the range of 254° C. and containing 17.7

per cent phosphorus. Cooling the second extract produced needle-shaped crystals which melted sharply at 240°-241° C. and contained 18.4 per cent phosphorus. These needles closely resembled the reaction product using paraformaldehyde both in appearance and melting point. A comparison of an infrared spectrum taken on this product by the potassium bromide technique. with a spectrum similarly obtained for the paraformaldehyde product showed that the two products were identical.

Reaction of Phenyldiamidophosphonamidate with Propionaldehyde in Chloroform.--Phenyldiamidophosphonamidate (7.8 g; 0.05 mole) and propionaldehyde (5.8 g.; 0.10 mole) were added to 60 ml. of chloroform and the mixture was stirred and refluxed for 24 hours. After cooling, the white solid was filtered, washed with excess chloroform, and air-dried to give 6.2 g. of a highly water-soluble product. This solid on recrystallization from hot 95 per cent alcohol gave long needles which melted sharply at 240°-241° C. A comparison of the infrared spectrum of this product with the spectra of the products obtained using both paraformaldehyde and benzaldehyde showed the compounds were identical.

Reaction of Phenyldiamidophosphonamidate with Chloroform.--To eliminate the possibility that the solvent rather than the aldehyde was responsible for the observed results, a reaction was run using only the chloroform. To 60 ml. of chloroform was added 3.9 g. of phenyldiamidophosphonamidate, and the mixture was stirred and refluxed for a period of four days. After four days, the solid was separated, washed with chloroform, and air-dried to give 3.25 g. of a solid which melted sharply at 187°-188° C. and did not depress the melting point of an authentic sample of original starting compound.

Reaction of Phenyldiamidophosphonamidate with Paraldehyde.--To 60 ml. of chloroform was added 7.8 g (0.05 mole) of phenyldiamidophosphonamidate and 13.2 g. (0.10 mole) of paraldehyde and the mixture was stirred and heated at reflux for 72 hours. After cooling, the white solid was separated, washed with chloroform, and air-dried to give 6.55 g. of product. The product was washed with water to remove any water-soluble salts. Evaporation of the water wash yielded no solid product. The solid was dried and found to melt sharply at 187°-188° C. and did not depress the melting point of an authentic sample of the starting compound.

Reaction of Phenyldiamidophosphonamidate with Diethyl Ketone in Chloroform.--Diethyl ketone (8.6 g.; 0.10 mole) was added to phenyldiamidophosphonamidate (7.8 g.; 0.05 mole) dispersed in 60 ml. of chloroform. The reaction was stirred and heated at reflux for 24 hours. After cooling, the white solid was filtered, washed with excess chloroform, and air-dried to a weight of 7.70 g. This solid was not water-soluble and could be recrystallized from hot 95 per cent alcohol to yield plates that melted at 187°-188° C. It did not lower the melting point of an authentic sample of the starting phosphonamidate.

Reaction of Phenyldiamidophosphonamidate with Paraformaldehyde in Absolute Ethanol.--In 60 ml. of absolute ethanol was placed 7.8 g. of phenyldiamidophosphonamidate and 3.0 g. of paraformaldehyde. The mixture was stirred and heated at reflux. The cloudy mixture started to clear up in about 60 to 70 minutes and at the end of 90 minutes was completely clear. The reaction was stopped and the liquor cooled. The liquor remained clear on cooling and was air-evaporated to yield a pasty solid mass which was extracted with four 75-ml. portions of hot carbon tetrachloride. The carbon tetrachloride product was then recrystallized seven more times from hot carbon tetrachloride to give some short needles that melted sharply at 134° C.

Anal. Calc. for $C_8H_{12}NPO_2$: C, 51.90; H, 6.53; N, 7.57; P, 16.73

Found: C, 52.26; H, 6.57; N, 7.66; P, 16.85

If this same reaction was not stopped after 90 minutes but was allowed to continue for three hours and the solution so obtained was concentrated to a small volume, it was possible to isolate a new product which could not be obtained from the 90-minute reaction. This new product came down as very long platelettes which melted at 217° C. after three further recrystallizations from absolute ethanol. The infrared spectrum showed the presence of a strong band in the 1450 cm^{-1} region which was not present in the above-mentioned compound.

Anal. Calc. for $C_8H_{14}NPO_3$: C, 47.28; H, 6.94, N, 6.90; P, 15.24

Found: C, 47.91; H, 6.53; N, 7.21; P, 15.25

Synthesis of Phenylethylphosphonamidate.--A separate synthesis of phenylethylphosphonamidate was undertaken to substantiate that this was, indeed, the product obtained in the 90-minute reaction described previously.

Preparation of Phenyldiethyl Phosphonite.--This preparation was essentially that described by Kosolapoff (55) and involved the reaction of phenyldichlorophosphine with ethanol in the presence of pyridine as a condensing agent. The use of ether as the solvent for the reaction greatly facilitated the separation of a pure product, since the pyridine hydrochloride formed was insoluble in the ether. In a liter flask was placed

450 ml. of anhydrous ether, 79.0 g. (1.0 mole) of pyridine and 46.0 g. (1.0 mole) of absolute ethanol. This solution was cooled at 0° C. and stirred while 89.0 g. (0.498 mole) of phenyldichlorophosphine (Eastman yellow label) was added slowly. The stirring was continued for one hour, after which the precipitated pyridine hydrochloride was filtered off and the liquor concentrated by removing the ether with water aspirator suction and a warm water bath. The concentrated liquor was fractionated to give a fraction weighing 49 g.; b.p. 86°-90° C. at 3 mm.; n_D^{20} 1.5121; reported: b.p. 235° C. at 760 mm., 110° C at 10 mm., calc. 86° C. at 3 mm.; n_D^{20} 1.5120.

Attempted Preparation of Phenylethylphosphonochloridate.--The procedure used for the preparation of this compound was similar to the procedure used by Gerrard (118) and by McCombie (119) for the preparation of phosphorochloridates. A chlorine cylinder was connected to a series of safety traps which were cooled by ice immersion. These safety traps were in turn connected to the reaction flask which was simply a 50 ml. filtering flask that had been fitted with a thermometer and a sintered glass inlet tube. This reaction flask was cooled by immersion in dry ice. Phenyldiethyl phosphonite (29.7 g.) was added to this flask and chlorine gas admitted very slowly while a temperature of -5° C. was maintained. The end of the reaction was ascertained when a yellow color appeared that did not disappear on shaking. At this point, the flask had gained 10.66 g. which corresponded exactly to the expected weight gain for the addition of one mole of chlorine to one mole of starting phosphonite. Air that had been dried by passage through sulfuric acid, phosphorus pentoxide, Drierite, and calcium chloride was then passed through the liquor for three hours. Next, 5 g. of lead carbonate was added slowly with shaking and the mass was allowed to stand overnight in a stoppered flask. Dry nitrogen was then blown through, a small amount of bone charcoal added, and the oily layer was filtered off. This oil was distilled under vacuum and a fraction boiling at 90° to 94° C. at 3 mm. was obtained. This clear oil had a fruity smell and did not react with silver nitrate solution after having been boiled with water. The negative chloride test indicated that the product was not the expected compound.

In a second attempt, the chlorinated product was prepared and heated until the bubbling of gases stopped. During the bubbling, copious evolution of chlorine occurred and the temperature rose to 100° C. The liquor was then cooled to 40° C. and vacuum distillation was attempted. Nothing distilled even at 280° C. (pot temperature) and 0.6 mm. and the very viscous syrup remaining produced a solid transparent mass on cooling. This mass resembled the polyphosphate glasses.

Preparation of Phenylethylphosphonamidate.--As mentioned above, attempts to isolate pure phenylethylphosphonochloridate were unsuccessful. However, if any of the desired phosphonochloridate had formed, it might be possible to utilize it without necessarily isolating it. A batch of chlorinated phenyldiethyl phosphonite was prepared and allowed to stand overnight. A 500-ml., three-necked flask was fitted with a stirrer, dropping funnel and a cold finger filled with dry ice-acetone mixture and was immersed in a dry ice-acetone bath. Ammonia gas was passed in until 100 ml. of liquid ammonia had collected in the flask, and 20 g. of the chlorinated phosphonite product was added in a dropwise manner. To the reaction 50 ml. of chlorofrom was added to act as a suspending agent for the pasty mass and the reaction further stirred and allowed to come to room temperature over a three-hour period. The white solid was filtered, washed with excess chloroform, and air-dried to give 9.7 g. of a water-soluble compound which gave a positive chloride test and was believed to be ammonium chloride. Evaporation of the chloroform layer gave a white flaky residue which was recrystallized from hot carbon tetrachloride three times to give a product which melted sharply at 134° C. The infrared spectrum of this compound, as run by the potassium bromide technique, was identical with the reaction product obtained by reacting phenyldiamidophosphonamidate with paraformaldehyde in absolute ethanol. Analysis showed that the product contained 16.70 per cent phosphorus as compared to 16.75 per cent theoretically required for the predicted product.

Reaction of Phenyldiamidophosphonamidate with Diethyl Ketone in Absolute Ethanol.--To 7.8 g. (0.05 mole) of phenyldiamidophosphonamidate dispersed in 50 ml. of absolute ethanol was added 8.6 g. (0.10 mole) of diethyl ketone, and the mixture was stirred and heated to reflux. It required 24 hours of refluxing for the reaction to yield a clear solution. The clear liquor was evaporated to a small volume on a steam bath and gave a liquor smelling strongly of diethyl ketone which yielded a solid product on standing. The solid so obtained was further purified by three recrystallizations from hot carbon tetrachloride to give a product which melted sharply at 134° C. and causedno melting point depression when melted with a sample of phenylethylphosphonamidate prepared by a separate route. The infrared spectrum of this compound was also identical with that of the phenylethylphosphonamidate.

Reaction of Phenyldiamidophosphonamidate with Absolute Ethanol.--To determine the effect of pure solvent on phenyldiamidophosphonamidate the following reaction was performed. Phenyldiamidophosphonamidate (7.8 g.) was added to 50 ml. of absolute alcohol and the mixture stirred at reflux for 30 hours. After cooling, the solid was filtered off, air-dried to a weight of 1.6 g., and shown to be unreacted starting material. The liquor was evaporated to give a solid which was recrystallized three times from hot carbon tetrachloride and produced crystals of 134° C. melting point. These crystals were shown by melting point depression and by infrared spectra to be identical with phenylethylphosphonamidate prepared by other methods.

Reaction of Phenyldiamidophosphonamidate with Paraformaldehyde in Methanol.--Phenyldiamidophosphonamidate (7.8 g.; 0.05 mole) and paraformaldehyde (3.0 g.; 0.10 mole) were added to 50 ml. of methanol and the reaction stirred at reflux. The mixture appeared to have reached a translucent stage in 100 minutes but some solid was still definitely present. After two hours, the reaction was stopped even though the solution had not cleared completely. The finely dispersed solid smelled strongly of formaldehyde after being filtered, and this gummy residue was air-dried overnight to give 1.0 g. of solid. The liquor was air-evaporated and gave a solid and an oil which had no formaldehyde odor. The oil crystallized when it was agitated and final traces of methanol were removed by heating on a water bath. The weight of the residue was 9.0 g. and this was extracted with four successive 75-ml. portions of hot carbon tetrachloride which on cooling yielded 2.2 g. of product. This product, on being recrystallized seven times from carbon tetrachloride, gave neeldes that melted sharply at 113° C.

Anal. Calc. for $C_7H_{10}NPO_2$: C, 49.12; H, 5.88; N, 8.20; P, 18.10

Found: C, 49.63; H, 5.84; N, 8.37; P, 18.15

Reaction of Phenyldiamidophosphonamidate with Methanol.--Five grams of phenyldiamidophosphanamidate was stirred and heated at reflux for 44 hours in 50 ml. of methanol that had been boiled under nitrogen to remove oxygen. At the end of this time, the flask was cooled, and the solid that remained was filtered off and air-dried to a weight of 3.85 g. This solid was shown to be starting compound through the melting point depression technique. The liquor was air-evaporated to give 0.9 g. of light yellow plates that smelled like laundry soap. After three 75-ml. extractions of this solid with hot carbon tetrachloride there remained 0.55 g. of yellow solid. The carbon tetrachloride on cooling yielded 0.35 g. of needle-shaped crystals that melted at 113° C. and did not depress the melting point of the product obtained by the use of paraformaldehyde.

Reaction of Phenyldiamidophosphonamidate with Paraformaldehyde in Propanol.--Eastman white label *n*-propyl alcohol was purified by distillation. To 60 ml. of this distilled propanol was added 7.8 g. of phenyldiamidophosphonamidate and 3.0 g. of paraformaldehyde and the reaction was stirred and heated to reflux. After refluxing for 70 minutes, the solution became clear and after 90 minutes the reaction was stopped. The liquor was filtered and air-dried to give a pasty mass that was extracted with successive portions of hot carbon tetrachloride. The carbon tetrachloride solutions on cooling yielded a product which was recrystallized seven more times to give crystals melting at 139° C.

Anal. Calc. for $C_9H_{14}NPO_2$: C, 54.30; H, 7.08; N, 7.03; P, 15.55

Found: C, 54.95; H, 7.19; N, 7.13; P, 15.60

Reaction of Phenyldiamidophosphonamidate with Propanol.--Five grams of phenyldiamidophosphonamidate was refluxed with 60 ml. of Eastman white

white label n-propanol previously distilled. After 18 hours of refluxing, the reaction was stopped and the solid was filtered off. This solid was air-dried to a weight of 4.7 g. , had a melting point of 187°-188° C., and did not depress the melting point of an authentic sample of the starting compound. The liquor was air-evaporated and gave a very little bit of solid which did not dissolve at all in hot carbon tetrachloride.

Phenyldianilidophosphonamidate

Preparation of Phenyldianilidophosphonamidate.--This compound can be readily prepared by reacting phenyldichlorophosphine oxide with excess aniline. A liter flask was filled with a solution of 200 g. of aniline dissolved in 300 ml. of chloroform and this liquor was stirred and maintained at 0° C. while 97.5 g. of phenyldichlorophosphine oxide was slowly added. The solid was filtered, washed free of excess aniline and recrystallized from hot 95 per cent alcohol to give a very fluffy white product that melted sharply at 213° C. The reported melting point for this product is 213° C. (72).

Reaction of Phenyldianilidophosphonamidate with Formalin.--Phenyldianilidophosphonamidate (3.1 g.; 0.01 mole) was placed in 40 ml. of water and 1.62 g. (0.02 mole) of 37 per cent formaldehyde was added. The reaction was stirred and heated at reflux for 24 hours. After cooling, the solid which remained was filtered, washed with more water, and air-dried to a weight of 3.0 g. This solid was shown to be starting compound by the use of the melting point depression technique.

Reaction of Phenyldianilidophosphonamidate with Paraformaldehyde in Chloroform.--One-hundredth of a mole of phenyldianilidophosphonamidate and two-hundredths of a mole of paraformaldehyde were placed in 60 ml. of chloroform and heated at reflux for 54 hours. At the end of this time, the remaining solid was filtered, washed with hot water to remove any formaldehyde, and air-dried. This solid was shown to be starting phosphonamidate and was recovered in 90 per cent yields.

Reaction of Phenyldianilidophosphonamidate with Paraformaldehyde in Absolute Ethanol.--Phenyldianilidophosphonamidate (0.01 mole) was added to paraformaldehyde (0.02 mole) in 70 ml. of absolute ethanol and the reaction was stirred and heated at reflux for 24 hours. At the end of this period, there was isolated 2.50 g. of unreacted solid which was shown to be unreacted starting phosphonamidate. Evaporation of the liquor yielded 0.50 g. of a light yellow-tinged solid. This solid was not further identified.

Analytical and Testing Procedures

Analytical Procedures

Sulfur.--The sulfur analyses were made using a Parr bomb fitted for electrical ignition. The cellulose samples were ground in a laboratory-size Wiley mill until the particles would pass through a 60 mesh screen. An accurately weighed 0.4-0.5 g. sample of the ground cellulose was placed in the bomb and mixed thoroughly with 1.0 g. of potassium perchlorate. The wire fuse then was attached to the ignition head. Approximately 15 g. of sodium peroxide was then added and mixed thoroughly, after which the bomb was assembled, tightened, and ignited. After cooling, the bomb was dismantled and the fusion cup placed in 100 ml. of warm water to dissolve the melt. The fusion cup was then removed and rinsed and the solution neutralized with concentrated hydrochloric acid. The solution was filtered, the filtrate was diluted to 400 ml., and 10 ml. of saturated bromine water was added. The solution was boiled to expel the liberated bromine and made neutral to methyl orange indicator with sodium hydroxide. The solution was heated, made acid by adding 1.0 ml. of hydrochloric acid, and the sulfate was precipitated by adding 10 ml. of 10 per cent barium chloride solution. After standing overnight, the precipitate was filtered, washed until it gave a negative chloride test, and ignited to a constant weight.

$$\text{Per cent Sulfur} = \frac{\text{weight of } BaSO_4 \times 13.74}{\text{weight of sample}}$$

Halogen.--The determination of halogen was made using the method described by Feldman and Powell (120) and modified by Umhoefer (121). A dry accurately weighed sample of between 0.15 g. to 0.30 g. was placed into 30 ml. of t-butyl alcohol. To this was added 1.5 to 2.0 g. of sodium metal which was enough so that there was some metallic sodium left at the end of the reflux. The liquor was refluxed for 2.5 hours, cooled, and the excess sodium was destroyed by adding slowly 20 ml. of 95 per cent ethanol. Finally, 70 ml. of water was added and sufficient ethanol to give a homogeneous solution necessary for accurate titration. The solution was neutralized with 6 N nitric acid, and the halogen content was determined by the Mohr titration procedure.

Nitrogen.--All nitrogen determinations conducted in the laboratory followed the standard Kjeldahl method (122).

Phosphorus.--The following method for the determination of phosphorus is evaluated and established in the appendix of this report. An accurately weighed sample of about 10 g. was placed into a 50 ml. pyrex test tube and five glass boiling beads were added to eliminate splattering of the liquid during subsequent heating. Concentrated sulfuric acid (5.0 ml.) was added and the test tube heated to SO_3 fumes. After cooling, 10 ml. of 30 per cent hydrogen peroxide was added in a dropwise manner and the tube was heated until SO_3 fumes appeared. This oxidation step was repeated and then 10 ml. of water was added and the liquor was again heated to SO_3 fumes. This latter step was included to insure any cleavage that may be facilitated by dilute rather than by concentrated acid. The oxidation step was repeated using only 5.0 ml. of the 30 per cent peroxide. The liquor was brought to SO_3 fumes twice using two separate 10 ml. portions of water in order to remove all of the excess peroxide. The solution then was neutralized with ammonium hydroxide, made acidic with 3.0 ml. of concentrated nitric acid, and adjusted to 250 ml. total volume. A 25.0 ml. portion of this solution was added to 75 ml. of water containing 15.0 g. of ammonium nitrate and 2.0 ml. of one per cent gelatin solution. This liquor was heated to 40° C. and 45 ml. of ammonium molybdate precipitating solution was added. The precipitating solution was prepared immediately before being used by adding 15 ml. of ammonium molybdate solution (prepared by mixing 400 ml. of water and 80 ml. of concentrated ammonium hydroxide and dissolving 100 g. of ammonium molybdate in this liquor) to 30 ml. of nitric acid (prepared by mixing 400 ml. of concentrated nitric acid with 600 ml. of water). The flask was shaken intermittently for 30 minutes, and the precipitate then was suction filtered through an asbestos matted gooch crucible prepared so as to have the thinnest possible asbestos matting. The precipitate was washed with 150 ml. of two per cent sodium nitrate, transferred quantitatively into the precipitating flask, and titrated with standard alkali.

$$\text{Per cent Phosphorus} = \frac{P}{25{,}000} \frac{(\text{m.e. of base}) \times 100}{\frac{\text{wt. of sample}}{10}}$$

Testing Procedures

Strength Tests.--All tests for the strength of the samples were made using standard textile testing equipment. The raveled-strip method and also the single end inclined-plane type tests were employed. The samples were conditioned for two days at 65 per cent relative humidity and 70° C. and tested as prescribed by ASTM standard procedures (123). Statistical evaluation of all results were made employing the "t" distribution method of comparing means as described by Dixon and Massey (124).

Viscosity Measurements.--The viscosity measurements were made using a series 300 Canon-Fenske type viscosimeter in a constant temperature bath at 32° ± 0.005° C. and employing 0.500 per cent solutions of cellulose in cupriethylene diamine. The cupriethylene diamine was prepared by the procedure described in the ASTM specifications (123), which require the solution to be 1.000 ± 0.005 M with respect to copper and contain a 2:1 mole ratio of ethylene diamine to copper. The solution thus prepared was also checked against a commercially available standard sample of cupriethylene diamine prepared by the Ecusta Paper Company, and was found to be acceptable in all respects. The actual values reported for viscosities are reported in terms of seconds (± 0.10 second) required for the flow of 10 ml. and so are on a relative rather than an absolute basis. This approach was sufficient in view of the fact that many samples could not be brought into complete solution.

CHAPTER IV

SUMMARY OF RESULTS

The study of the production of short cross-links in cellulose was tried with both oxalyl and phosphoryl chloride. In the reaction of phosphoryl chloride with soda cellulose at low temperatures, only small amounts of phosphorus were introduced. These small amounts of phosphorus were sufficient to cause the sample to be of limited solubility in cupriethylene diamine. A sample so prepared was considerably weakened even though the phosphorus is expected to be doubly bonded as was found for the use of pyridine catalyst. The only logical way to explain this total behavior is to postulate an internal 7-membered diester involving the 6 and 3 positions of the anhydroglucose unit.

The attempts to introduce unsaturation into the anhydroglucose unit were fundamentally sound but, as is the case with many reactions of cellulose, were probably inhibited by the solid nature of the cellulose. The use of spongy regenerated cellulose was also found to have little effect.

The solid nature of the cellulose can also be considered as the factor limiting the reaction of cellulose with phosphonimides and phosphites. In the case of halomethylphosphonic acid and its derivatives, the lack of reactivity is attributable to the lack of activation of the halogen. This points up very significant fundamental differences between phosphoryl and carbonyl structures. The reaction of soda cellulose with aryl rather than alkyl phosphites is explained by the fact that the aryloxy group is a far better leaving group than an alkoxy group. For the cellulose phosphite obtained by the reaction of soda cellulose with triphenyl phosphite, the change on standing is not readily explicable. The lack of reaction of the product with reagents that react rapidly with trivalent phosphorus compounds would lead to the conclusion that the phosphorus is no longer trivalent. A possible explanation of this action is that one of the phenoxy groups has been replaced by a hydroxyl group. There is considerable evidence that the (OH) group on a phosphite rearranges to give H - P(O) structures. This would explain the fact that the cellulose was no longer basic since such compounds are acids and would also explain the lack of reaction with iodine, sulfur, and peroxide. In any case, it is most probable that the reaction of cellulose with triphenyl phosphite involves more than the simple displacement of phenoxy by a basic cellulose structure.

The reaction of diamidophosphoramidates with formaldehyde represents a valuable procedure for preparing phosphorus containing resins. The far more facile reaction obtained by the use of phenyldi(methylamido)phosphoramidate and the lack of reaction obtained by the use of phenyldianilidophosphoramidate in place of phenyldiamidophosphoramidate demonstrates that the nitrogen atom is involved in the reaction. The extreme differences in reactivity of and the products obtained from the Ph - O - P structures as compared to Ph - P structures illustrates that stability of the phosphorus-nitrogen linkage is enhanced by the addition of inductive groups. In view of these results, it can be predicted that the most stable P - N linkage would be found in structures containing two (RO) groups and only one nitrogen group. The syrups obtained from the reactions of the phosphoramidates with aqueous formaldehyde and the films obtained from the corresponding reactions in chloroform are thought to be reaction products involving formaldehyde and not simply hydrolysis products. Although such products have no formaldehyde odor and give no test for free formaldehyde, they do liberate formaldehyde on treatment with sodium hydroxide solutions.

The study of the reactions of diamidophosphonamidates was most informative in illustrating several features of such compounds. The extremely rapid and vigorous reaction of the diamido compound with aqueous formaldehyde can be readily interpreted as signifying that the nitrogen atoms have considerable amine character. Since a two-step mechanism involving initial hydrolysis can be discounted on the basis that water alone did not hydrolyze the compounds and since dianilido structures were found to be unreactive under all conditions tested, it must be concluded that the nitrogen atom is involved directly in the reaction. This reaction then provides direct experimental evidence for high-electron density on nitrogen. This could not be expected if the nitrogen electrons entered into resonance with the phosphorus atom. Further, in comparing $PhOP(O)(NH_2)_2$ with $PhP(O)(NH_2)_2$, resonance interaction of the phenoxy oxygen would predict that the nitrogens in the PhOP structure would be more basic. Since the exact opposite is true experimentally, it must be concluded that inductive effects are more important.

It has been shown that the reactions of $PhP(O)(NH_2)_2$ are accelerated by aldehydes but are essentially unaffected by ketones. Moreover, the nature of the aldehyde can vary over a wide range and the aldehyde itself is not part of the reaction product. This is illustrated by the fact that paraformaldehyde, benzaldehyde, and propionaldehyde could all be used effectively and all produced the same reaction product. The reaction definitely requires a ratio of paraformaldehyde to diamidophosphonamidate that is greater than 1:1 since this ratio was found to leave much of the phosphorus compound unreacted. A 2:1 mole ratio of aldehyde to phosphorus compound was employed in all reactions even though this may well represent a slight excess of aldehyde. There can be little doubt that the solvent enters into the reaction and a very systematic picture was produced by using various solvents. In water, the (OH) was found to be substituted for the (NH_2) groups. In ethanol, (OEt) substituted for an (NH_2) and in methanol and propanol it was found that (OMe) and (OPr) respectively were substituted for an (NH_2) group. In all cases, except ethanol, the reactions would not proceed without the presence of added aldehyde.

In chloroform where there is no good replacing group readily available, it appears as if the polar oxygen of the phosphoryl group exerted an attacking influence and formed a "pyro" linkage. In the case of using ethanol and longer reaction periods, it was found that the second (NH_2) group was replaced by an (ONH_4) group. This could only arise by water hydrolysis of the second (NH_2) group and is important in explaining the specific action of aldehydes. It appears that the nitrogen and the aldehyde react to form an (OH) specie which then exerts its attacking effect. The simplest mechanism is one similar to that proposed for the formation of Schiff's bases. This does not exclude the possibility that in all cases a common intermediate is formed which then further reacts with solvent. The more stable nature of the second (NH_2) group is in accord with the stabilizing affect to be expected for the introduction of an (OR) group.

The product obtained from the use of chloroform solvent deserves special mention. In this case, two insoluble solid compounds reacted to produce a third more insoluble compound. The analytical results signify a 1:1 phosphorus to nitrogen ratio, yet a 10 per cent solution of this compound in water is completely neutral to litmus. The nitrogen is present in the form of an ammonium salt as is indicated by the rapid formation of an insoluble silver salt which contains no nitrogen and also by infrared spectral data. The instantaneous formation of a nitrogen free precipitate on adding hydrochloric acid to a water solution is also consistent with an ammonium structure. The extended hydrolysis of this precipitate to produce pure phenylphosphonic acid exclusively is important. All of these data are in agreement with only one possible type of structure: that of a pyrophosphonate. The preparation of phenyldiammoniumpyrophosphonate by this described technique should, therefore, be considered as unique, since such structures are not readily available by presently known schemes.

The difficulty of obtaining pyrophosphonic acid structures is best illustrated by the many unsuccessful attempts that were made to prepare such structures by a separate synthetic procedure. The controlled hydrolysis of the corresponding phosphonyl dichloride, the reaction of the phosphonyl dichloride with the free acid, and high temperature dehydrations were found to be incapable of producing the desired product.

The use of the potassium bromide pellet technique of obtaining infrared spectra of solids proved to be a most potent and valuable method for the identification and confirmation of the various chemical structures.

The lack of reactivity of the halomethylphosphonic acid compounds and the effects of substituent groups on the reactivity of adjoined nitrogen atoms has definitely indicated that the nature of the phosphoryl linkage is not in accord with the usually advocated mesomeric interpretations. The proposed explanation of the nature of the phosphoryl linkage is capable of predicting changes to be expected in reactivity on alteration of the compound structure, and is in accord with the physical data.

CHAPTER V

CONCLUSIONS

Several conclusions can be drawn on the basis of these experimental results.

1. Aryl phosphites react with soda cellulose to give a product having radically different properties.
2. The halogen of halomethylphosphonic acid is activated by the phosphoryl group far less than the amount that the halogen of haloacetic acid is activated by the carbonyl group.
3. Diamidophosphoramidates can be reacted with formaldehyde to produce resin products whose properties can be modified by the use of different groupings. The speed of the reaction is determined by the nature of the nitrogen atom employed and is increased by N-methyl substituents and decreased by N-phenyl substituents.
4. The P - N linkages of phenyldiamidophosphonamidates are relatively weak due to the fact that little, if any, resonance interaction takes place between the atoms.
5. The nitrogen atoms of phenyldiamidophosphonamidates have considerable amine character as evidenced by vigorous reaction with formaldehyde, lack of amide type stabilization by the phosphoryl group, and spectral data.
6. Controlled replacement of the (NH_2) groups of phenyldiamidophosphonamidate can be effected to produce both alkoxy-and pyro-type

structures. The preparation of the pyro structures by this route represents a unique new synthesis of such compounds.

7. The available experimental evidence, including some of the reactions presented in this dissertation, and theoretical considerations disprove many analogies that may be thought to exist between phosphoryl and carbonyl structures and it is concluded that the $P = O$ symbolism is not only misleading but is incorrect.
8. The proposed interpretation of the nature of the phosphoryl linkage is capable of predicting changes in reactivity on alteration of compound structure and is in agreement with physical data.

CHAPTER VI

RECOMMENDATIONS

The following recommendations for future research are made.

1. The reaction of carbodiimides and phenylphosphonic acid should be attempted to provide a separate synthesis for phenyldiammoniumpyrophosphonate.
2. On the basis of the proposed mechanism for the above reaction, the reaction of cellulose with thiourea and various monohydric phosphorus compounds should be investigated. This reaction appears to provide a route to the production of a whole range of cellulose phosphates.
3. The reaction products of various diamido and monoamidophosphoramidates with formaldehyde should be investigated for possible use in the textile field. In synthesizing and reacting the various compounds, the effect of structure on reaction rate and product stability should be particularly noted to determine if it is in general agreement with the results predicted on the basis of arguments put forth in this dissertation.
4. The reaction of phenyldiamidophosphonamidate with aldehydes should be further studied using various substituents and determining their effect on the reaction. The use of various new solvents should be employed to extend the general usefullness of the reaction. The possibility of using phosphonamidates with cellulose as the alcohol should definitely be investigated.

APPENDICES

APPENDIX I

INFRARED SPECTRA

General Assignments

In recent years several studies have been performed which have led to assignments for characteristic phosphorus bands in the infrared region (99, 109, 110).

P(O) Linkage.--A rather extensive study performed by Daasch and Smith (99) shows that a strong phosphoryl oxygen band appears in the 1250-1300 cm^{-1} region if the oxygen is unbonded and in the 1200-1250 cm^{-1} region if the oxygen is hydrogen-bonded. This band is little affected by the type of compound involved but was found to shift consistently to higher wave numbers in the presence of electron withdrawing groups. It is significant in such a correlation to mention that alkoxy groups act similar to halo substituents and behave as electronegative withdrawing groups.

The effect of the alkoxy groups on the hydrogen bonding ability of the phosphoryl oxygen was also studied by others. Geddes (100) demonstrated that triphenyl phosphine oxide, $(Ph)_3P(O)$, has a more negative oxygen and thus possesses greater hydrogen bonding tendencies than does triphenyl phosphate, $(PhO)_3P(O)$. Kosolapoff and McCullough (101) studied the heats of mixing of various phosphorus compounds with chloroform and found that hydrogen bonding tendencies of the phosphoryl oxygen decreased in the order $R_2P(O)(OR') > RP(O)(OR')_2 > (RO)_3P(O)$. Finally, Halpern (102) has studied the position of the C - H and the P(O) absorption bands of $CHCl_3$, $CHCl_2CCl_3$, and $CHCl_2CHCl_2$ in CCl_4 solution using $P(O)Cl_3$, $(EtO)_3P(O)$, and

$(n\text{-}C_4H_9)_3P(O)$. It was found that the C - H and the P(O) absorptions shifted to lower frequencies. The magnitude of the shifts decreased in the order $(n\text{-}C_4H_9)P(O) > (EtO)_3P(O) > P(O)Cl_3$, indicating the electron withdrawing capacity of the substituent groups.

Ph-P Linkage.--A study (99) of compounds containing the phenyl-phosphorus linkage has established that this linkage is characterized by two sharp bands of medium intensity: one is located in the 1435-1450 cm^{-1} region while the other is in the 995-1005 cm^{-1} region. These bands represent the presence of a phenyl group whether the usual sharp bands associated with benzene ring stretching at 1500 cm^{-1} and at 1600 cm^{-1} are predominant or not. The weak benzene bands in the 1650-2000 cm^{-1} region and the strong C - H deformation bands in the 650-750 cm^{-1} region (that are attributed to varying numbers of adjacent hydrogens on the ring, and so are valuable in determining the number and position of substituent groups) are still present.

P - O - C Linkage.--General assignments for aryloxy and alkoxy groupings have been made (125). The aryloxy group linked to phosphorus gives rise to a strong absorption band in the 1190-1240 cm^{-1} region while an alkoxy grouping similarly linked absorbs strongly in the 1000-1050 cm^{-1} region. Specific additional band correlations have been assigned if the alkoxy constituent involves either the methyl or the ethyl grouping. The consistent appearance of a weak but well-defined band at 1190 ± 3 cm^{-1} has been noted for methyl groups. This band in conjunction with the more general P - O -C (alkyl) band in the 1000-1050 cm^{-1} region constitutes good evidence for the presence of a $P - O - CH_3$ linkage. The appearance of a sharp but weak absorption at 1160 ± 3 cm^{-1} in 70 compounds containing only a P - O - Et link in common has led to the assignment of this band to such a structure. This assignment is invalidated in the presence of P - O - Aryl groupings since a similar but considerably stronger band appears in this region. The use of this band in conjunction with the P - O - Aryl band at 1200 cm^{-1} or the P - O - Alkyl band at 1030 cm^{-1} can serve to establish which grouping is involved.

P - O - P Linkage.--It has been suggested by Bergmann (126) that absorption in the 930-970 cm^{-1} region can be associated with the P - O - P vibrations. Holmstedt and Larsson (110) have further suggested that absorption in the 710 cm^{-1} region can be associated with the P - O vibrations of a pyrophosphate linkage. Because of the very limited number of compounds considered, these assignments are not sufficient for determining the presence or absence of a P - O - P type structure.

P - NR'R" Linkage.--Amides of carboxylic acids display two well-established absorptions; one in the 3400-3500 cm^{-1} region attributed to N - H stretching and the other in the 1600 cm^{-1} region attributed generally to N - H deformation. Primary amides display two N - H stretching bands in the 3400-3500 cm^{-1} region and one strong deformation band in the 1620-1650 cm^{-1} region, which is commonly referred to as the amide II band. Secondary amides display one stretching band in the 3400-3440 cm^{-1} region, and the amide II band is shifted to the 1515-1570 cm^{-1} region but remains as a strong band. By comparison, amines display a somewhat different behavior. Primary amines display two absorption bands in the 3300-3500 cm^{-1} region and a strong N - H deformation band in the 1590-1650 cm^{-1} region. Secondary amines give rise to a single stretching band in the 3300-3500 cm^{-1} region, but the deformation band in the 1550-1600 cm^{-1} region is of such diminished intensity that it cannot usually be detected with the sample thicknesses normally employed.

This difference between the N - H deformation band for secondary amines and the secondary amides is pointed out so that proper comparison of these systems with the "phosphoramides" can be made. Studies have been carried out on phosphorus-nitrogen compounds by Bellamy and Beecher and by Holmstedt and Larsson (110, 111). The results of these studies point out that the N - H deformation and stretching bands are affected slightly by the presence of the phosphorus atom and occur at almost the same position as in normal amines. An interesting and very significant fact, however, is noted with secondary phosphoramides. Whereas P - NH_2 compounds display the expected N - H stretching bands in the 3300-3500 cm^{-1} region and the N - H deformation band in the 1550-1580 cm^{-1} region, P - NHR compounds exhibit only a stretching band in the 3300-3500 cm^{-1} region; the deformation absorption in the 1550 cm^{-1} region is of negligible intensity. This behavior closely parallels the behavior of the aliphatic amines. In anilido phosphorus compounds, the characteristic C - N stretching generally associated with aromatic amines is shown in the usual 1280 cm^{-1} region and interferes with the resolution of the phosphoryl oxygen band.

Preparation of the Infrared Spectra

All spectra were obtained using a Perkin-Elmer Model 21 Infrared Spectrophotometer set up as follows: resolution, 9/27; response, 2-2; gain, 5; speed, 5; automatic suppression, 4; scale, 1:1; light intensity, 0.34.

The spectra of all solids were obtained through the use of a potassium bromide pellet technique. Potassium bromide was ground until it passed through a 360 mesh screen. The sample was also ground until it would pass through the screen. To 0.100 g. of the potassium bromide powder then was added 0.0010 g. of the ground compound (one per cent of the potassium bromide) and the two solids were ground together to insure even and intimate mixing. This sample then was evenly spread in a 0.500 inch die form on a hydraulic press, tamped firmly, and pressed into a pellet form under 35,000 pounds pressure. The pellets so produced were placed into an adapter on the infrared spectrophotometer and were used to produce the curves. Certain compounds that were studied appeared to have an inherent property of producing pellets that were somewhat translucent and not absolutely clear. Pellets which were found to be somewhat opaque to infrared rays did not present exceptional problems, since a method was developed to overcome a considerable amount of such opacity. This method essentially consisted of placing a wire screen in the path of the reference light beam. This screen reduced the intensity of the reference beam sufficiently so as to make it comparable to the reduced amount of light penetrating through the sample.

The spectra of liquids were made by standard methods using 0.25 mm. cells. Spectra of polymers were made by depositing a thin layer of the polymeric solution on a clear potassium bromide pellet and heating the pellet in an oven to eliminate solvent. The spectra of syrups were made by placing the syrup between two clear potassium bromide plates. This latter technique has proved valuable for rapid examination of a large number of samples, for preliminary study of new substances, and for repeated checks on similar substances such as samples removed at various stages in a reaction.

Specific Assignments (cm^{-1})

Fig. 1 Phenyldiamidophosphoramidate, $PhOP(O)(NH_2)_2$.--

Phenyl	1590, 1485, 765, 690
Ph-O-P	1228
NH_2	3100, 1562
P(O)	1160

Fig. 2 Phenyldi(methylamido)phosphoramidate, $PhOP(O)(NHCH_3)_2$.--

Phenyl	1585, 1482, 755, 690
Ph-O-P	1213
NH	3130
CH	2960, 2850, 1450
CN	1418
P(O)	1190

Fig. 3 Phenyldiamidophosphonamidate, $PhP(O)(NH_2)_2$.--

Phenyl	1591, 1480, 743, 693
Ph-P	1433, 998
NH	3120, 1560
P(O)	1156

Fig. 4 Phenylphosphonic Acid, $PhP(O)(OH)_2$.--

Phenyl	1590, 1480, 751, 691
Ph-P	1435, 998
P-OH	2600-2700, 2100-2200
P(O)	1140

Fig. 5 Iodomethyldiethylphosphonate, $ICH_2P(O)(OEt)_2$.--

CH	2925, 1440
CH_3-C	1382
P(O)	1250
P-O-Et	1160
P-O-Alky	1025

Fig. 6 Phenyl(N-Phenyl)phosphonimide, $(PhP(O)NPh)_2$.--

Phenyl	3030, 1930, 1835, 1785, 1685, 1600, 1492, 750, 688
Ph-P	1440, 1001
C-N	1272
P(O)	1250

Fig. 7 Reaction Product of Phenyldiamidophosphoramidate with Paraformaldehyde in Chloroform (film).--

Phenyl	1600, 1492, 765, 690
Ph-O-P	1243
P(O)	1192
C-H	2860, 1455
NH	3160, 1565 (shoulder)

Fig. 8 Reaction Product of Phenyldi(methylamido)phosphoramidate with Formalin in Water (syrup).--

Phenyl	1580, 1478, 760, 690
Ph-O-P	1240
P(O)	1210
C-H	2950, 2825, 1450
N-H	3160
C-N	1418 (greatly diminished over original phosphoramidate)

Fig. 9 Phenyl(monoammonium)phosphonic Acid, $PhP(O)(OH)(ONH_4)$.--

Phenyl	1598, 747, 698
P(O)	1140
P-OH	2750, 2250-2450
NH_4^+	3000-3200, 1400-1470

Fig. 10 Phenyl(diammonium)pyrophosphonic Acid, $(PhP(O)(ONH_4))_2O$.--

Phenyl	1598, 737, 693
Ph-P	1435, 1000
P(O)	1220
NH_4^+	3000 (broad), 1400-1470 (broad)

Fig. 11 Silver Salt of Phenylpyrophosphonic Acid.--

Phenyl	3030, 1598, 1480, 732, 693
Ph-P	1439, 998
P(O)	1230
NH_4^+	not present

Fig. 12 Phenylethylammoniumphosphonate, $PhP(O)(OEt)(ONH_4)$.--

Phenyl	1590, 744, 693
Ph-P	1440
P(O)	1185
P-O-Alkyl	1048
CH_3-C	1383
NH_4^+	3000 (broad), 1465

Fig. 13 Phenylethylphosphonamidate, $PhP(O)(OEt)(NH_2)$.--

Phenyl	3080, 1590, 1470, 750, 693
Ph-P	1438, 995
P(O)	1196

NH_2	3220, 3180, 1563
C-H	2860, 2940
CH_3-C	1382
P-O-Alkyl	1035
P-O-Et	1157

Fig. 14 Phenylmethylphosphonamidate, PhP(O)(OMe)(NH_2).--

Phenyl	3040, 1585, 1475, 752, 699
Ph-P	1435, 995
NH_2	3200, 3140, 1560
C-H	2870
P-O-Alkyl	1032
P(O)	1190 (this band blocks identification of the weak P-O-Me band)

Fig. 15 Phenylpropylphosphonamidate, PhP(O)(OPr)(NH_2).--

Phenyl	3050, 1588, 1475, 750, 693
Ph-P	1432
NH_2	3200, 3140, 1552
P(O)	1200
CH_3-C	1380
n-propyl	832
P-O-Alkyl	1040 region

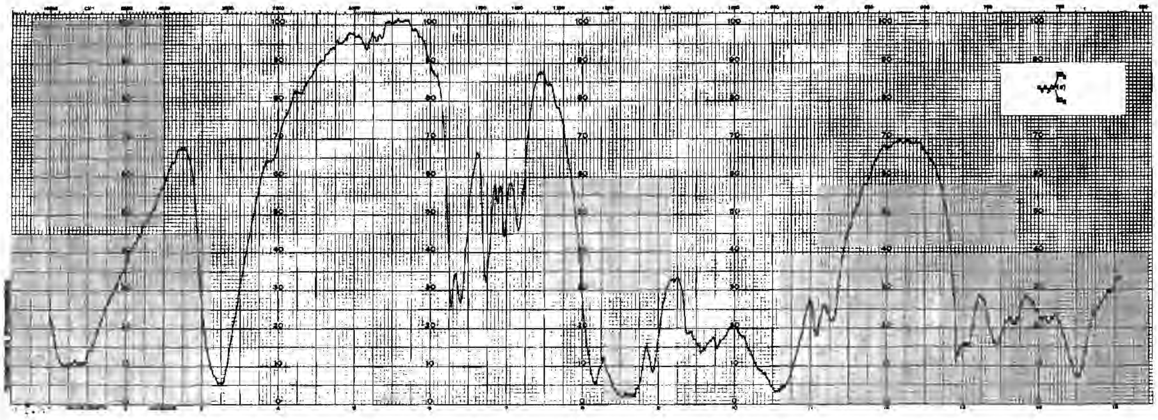


Fig. 1. Phenyldiamidophosphoramidate

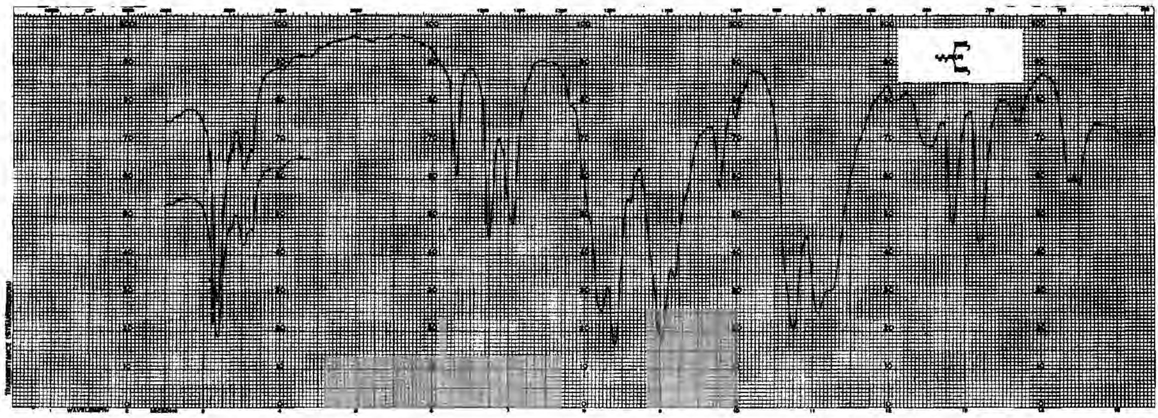


Fig. 2. Phenyldi(methylamido)phosphoramidate

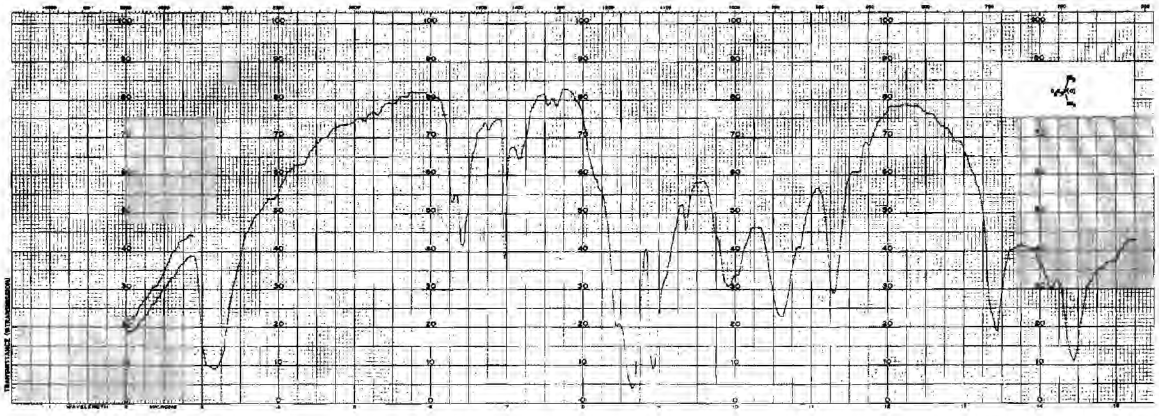


Fig. 3. Phenyldiamidophosphonamidate

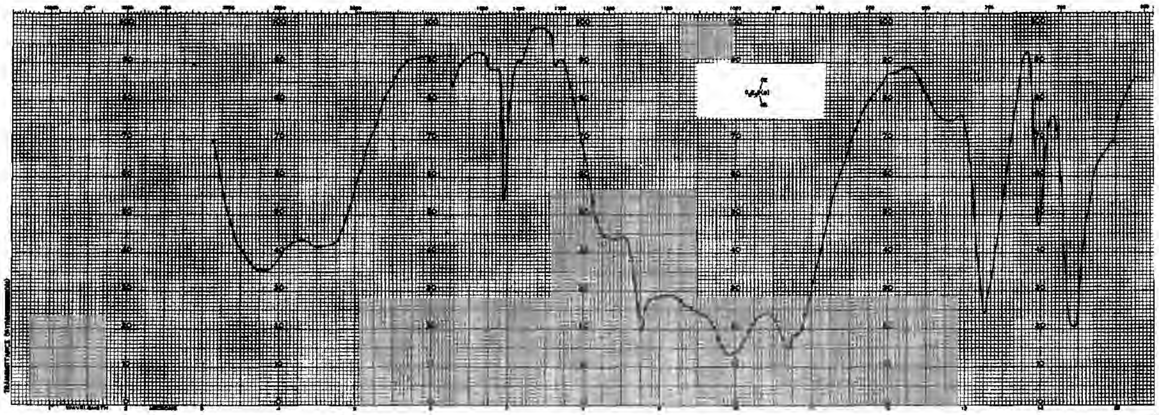


Fig. 4. Phenylphosphonic Acid

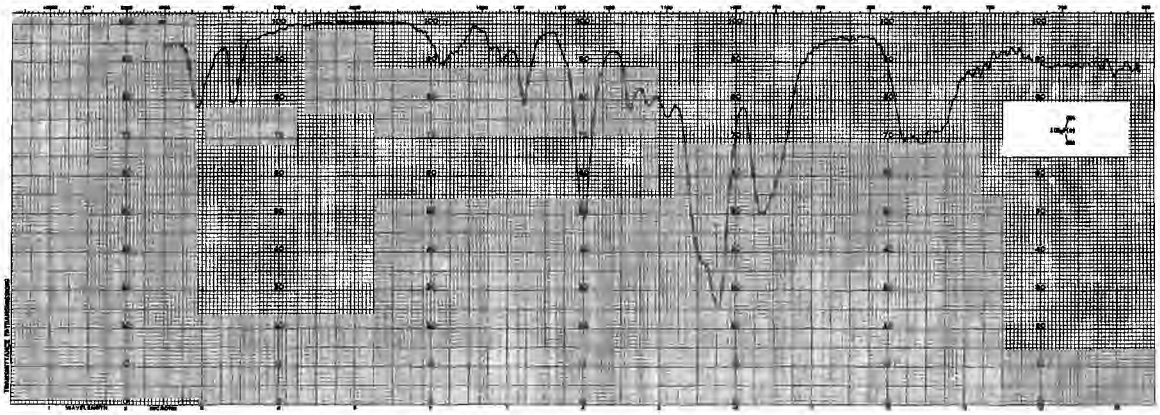


Fig. 5. Iodomethyldiethylphosphonate

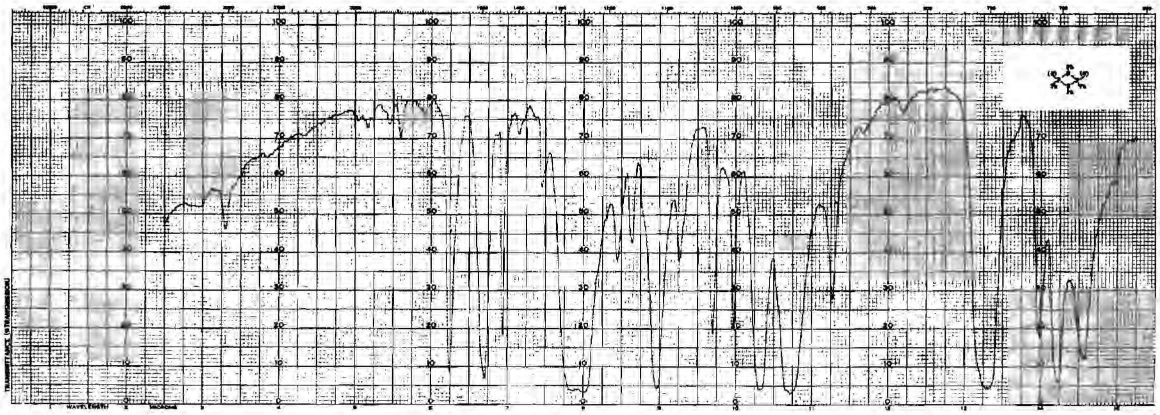


Fig. 6. Phenyl(N-phenyl)phosphonimide

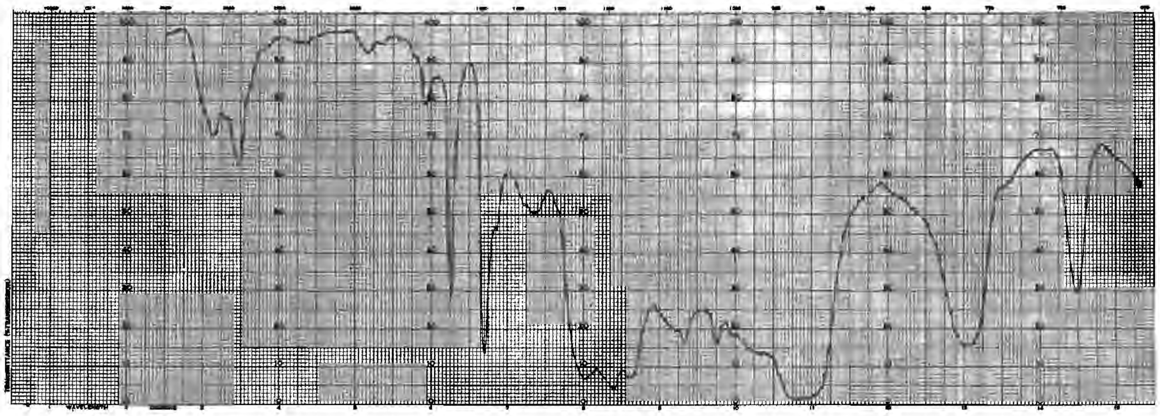


Fig. 7. Reaction Product of Phenyldiamidophosphoramidate with Paraformaldehyde in Chloroform

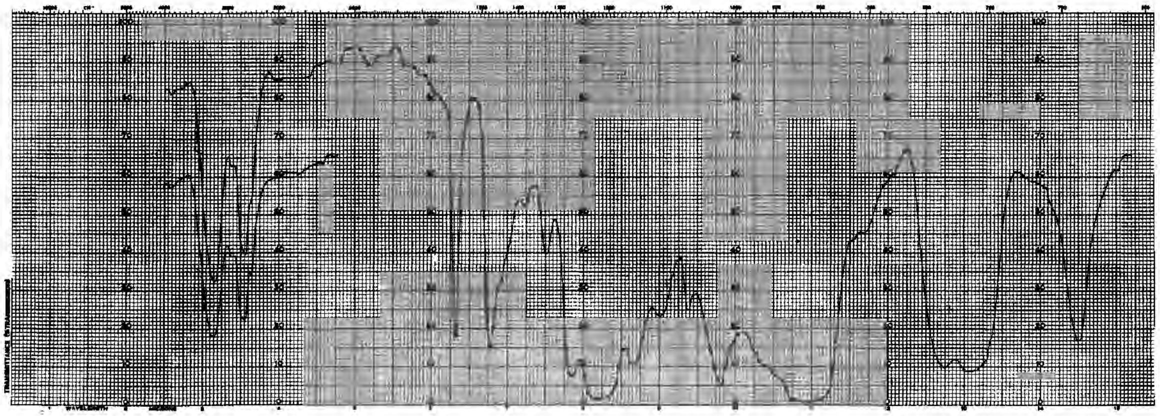


Fig. 8. Reaction Product of Phenyldi(methylamido)phosphoramidate with Formalin in Water

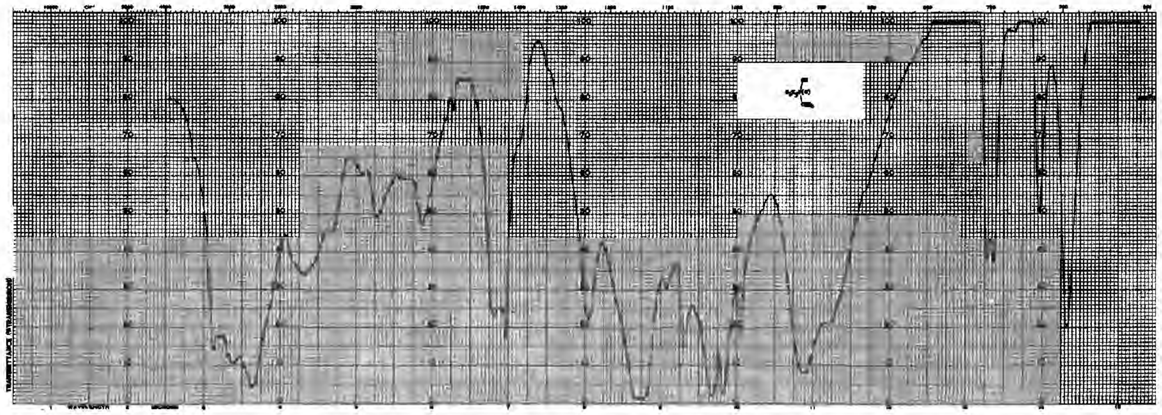


Fig. 9. Phenyl(monoammonium)phosphonic Acid

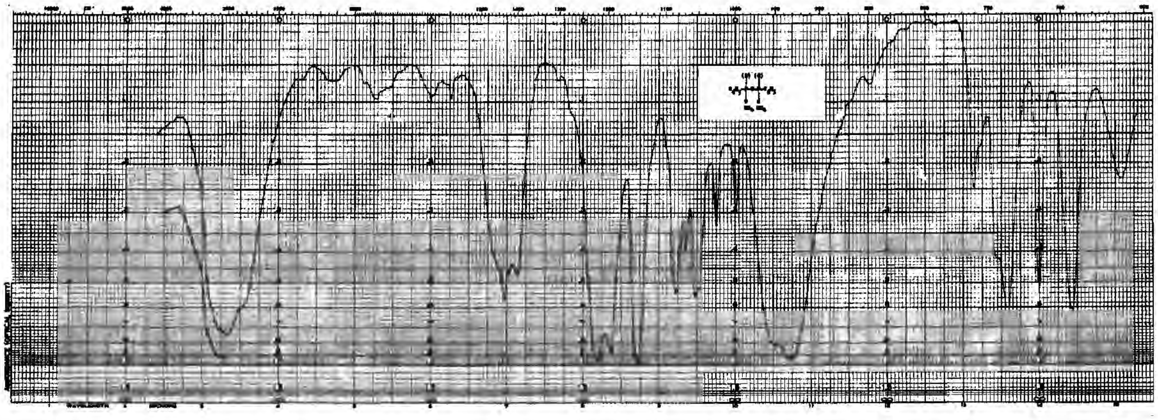


Fig. 10. Phenyl(diammonium)pyrophosphonic Acid

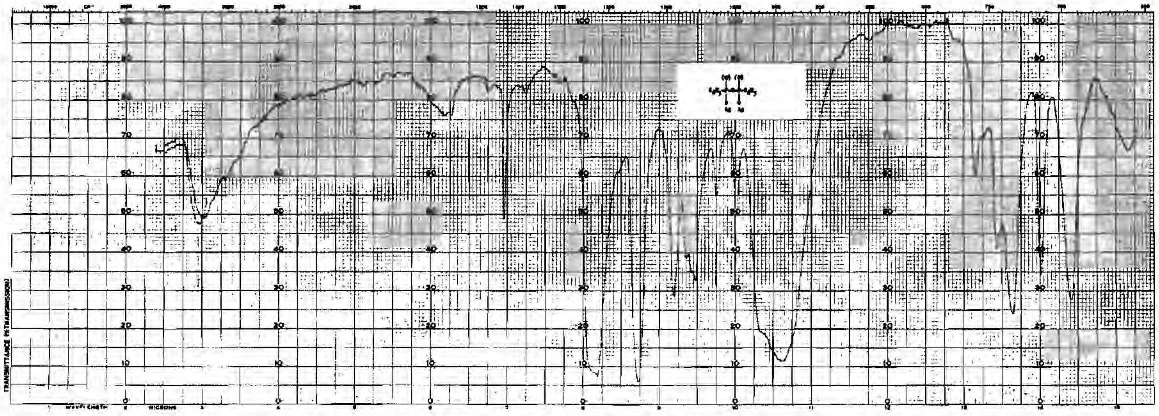


Fig. 11. Silver Salt of Phenylpyrophosphonic Acid

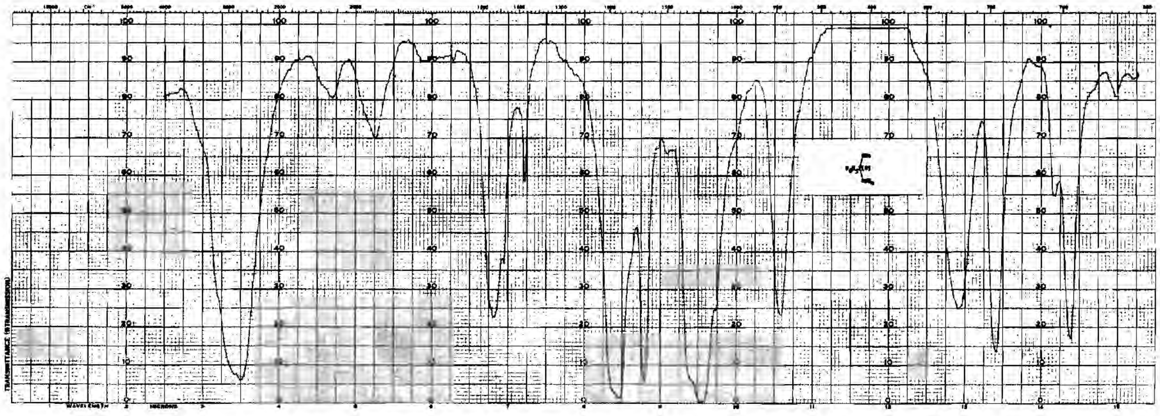


Fig. 12. Phenylethylammoniumphosphonate

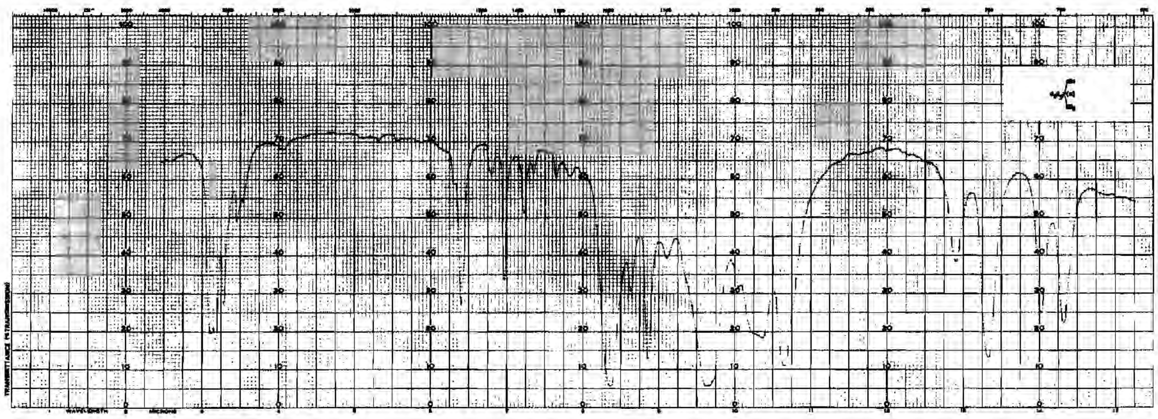


Fig. 13. Phenylethylphosphonamidate

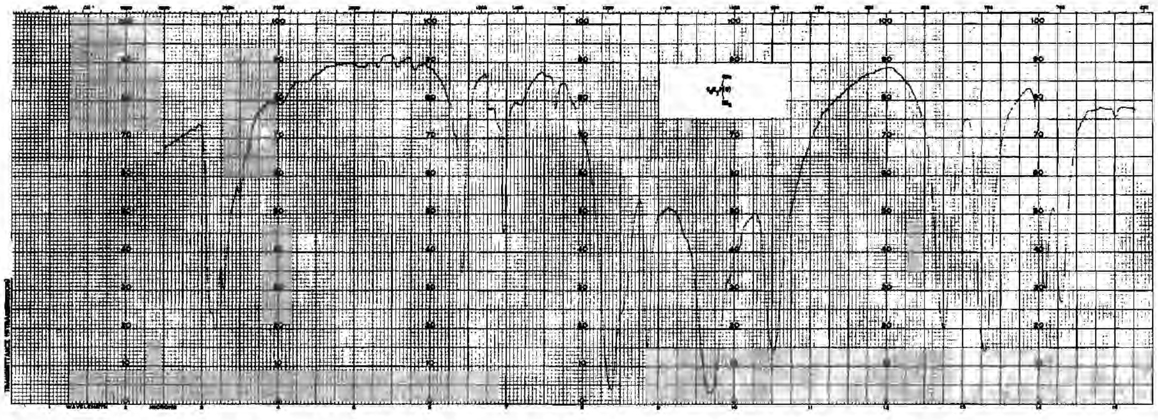


Fig. 14. Phenylmethylphosphonamidate

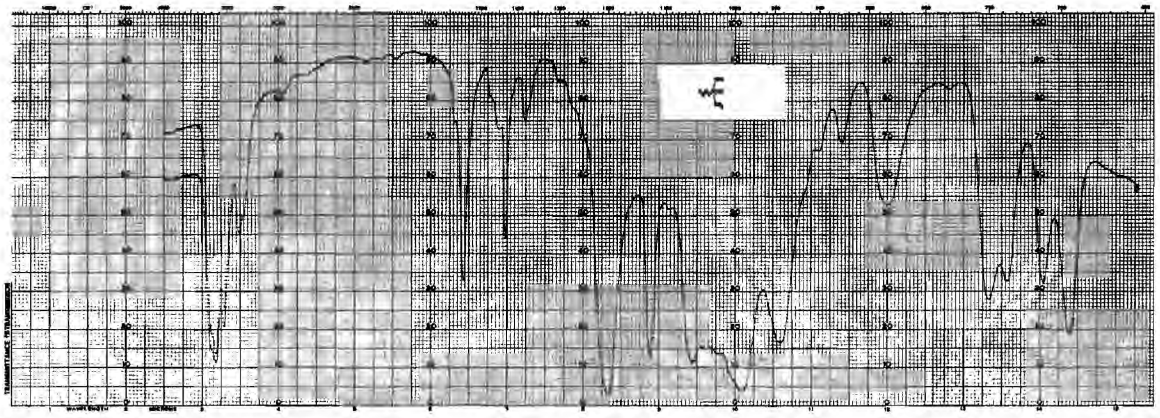


Fig. 15. Phenylpropylphosphonamidate

APPENDIX II

EVALUATION OF PHOSPHORUS DETERMINATIONS

Analyses of various compounds for phosphorus content by the conventional semi-micro methods were found to be unreliable. Hence, considerable effort was made to develop a rapid reproducible method of analysis. The limitations of these conventional methods are described as follows.

Nitric Acid Digestion.--The use of sulfuric acid-nitric acid digestion is commonly referred to (122), but this method was found to be inapplicable to this research. Phenyldiamidophosphonamidate, $PhP(O)(NH_2)_2$, which is known to have 19.88 per cent phosphorus, analyzed for only 5.65 per cent phosphorus when digested for 8 hours by this technique. This method may be of value as a sealed-tube digestion procedure, but is not acceptable for use as an open-beaker oxidation.

Molybdenum Blue Method.--The use of a technique employing sulfuric acid-sodium peroxide oxidation followed by the formation of a molybdenum blue complex with subsequent estimation of the phosphorus content by colorimetric comparison (127) was investigated. The method was found to suffer from the delicate nature of the blue complex and so is of limited reliability.

The necessary reagents for this technique are:

1. sulphuric acid; 15 ml. diluted to 100 ml. with water,
2. 5 per cent ammonium molybdate solution,
3. reducing agent; 0.25 g. of quinol and 7.5 g. of sodium sulfite made up to 50 ml. with water, and

4. potassium dihydrogen phosphate solution
   (1 ml. = 0.00007968 g. of phosphorus); 0.0350 g. of salt diluted to 100 ml. with water.

The standard comparison solution was made by diluting one cubic centimeter of the potassium dihydrogen phosphate solution to slightly less than 10 ml. with water and adding the same amount of sulphuric acid and molybdate as to the test sample. One milliliter portions of the reducing agent were added simultaneously to the test solution and to the standard solution. The volumes were then quickly adjusted to exactly 15 ml. and, after 30 minutes, the solutions were compared colorimetrically. A quantity of compound containing about 0.008 g. of phosphorus was weighed accurately to six decimal places, placed in a 20-ml. pyrex test tube with 2.5 ml. of sulphuric acid, and heated until charring set in. After cooling, four drops of 30 per cent hydrogen peroxide were added, and the tube was heated again. The oxidation was completed by using two more drops of the 30 per cent hydrogen peroxide. Any excess peroxide was then destroyed by treating twice with 2.0-ml. portions of water and evaporating to 0.50-ml. volumes. The contents of the tube were then transferred to a measuring cylinder, and 11.0 ml. of water, 2.0 ml. of ammonium molybdate, and 1.0 ml. of reducing solution was added and the volume was adjusted to 15.0 ml. total. After 30 minutes, the solution was compared with the standard using a Dubosque colorimeter. The blue color is claimed to depend on the reduction of the phosphomolybdic acid to the blue $22MoO_3 \cdot 2MoO_2 \cdot P_2O_5 \cdot H_2O$ acid.

Permanganate Oxidation Method.--This method was first suggested by Marie (128) and involves solution of the compound in concentrated nitric acid followed by oxidation with solid potassium permanganate. The excess permanganate and the manganese dioxide formed are reduced either with sodium sulfite or sodium nitrite and the phosphorus is then determined.

One gram of the compound was heated in 20 ml. of nitric acid and small portions of finely pulverized potassium permanganate were added until the solution remained distinctly red for several minutes. This should require about six times the weight of permanganate as the weight of the sample employed. After cooling, a 10 per cent solution of sodium nitrite was added dropwise until the dark brown manganese dioxide precipitate disappeared and the solution cleared completely. The solution was heated to expel oxides of nitrogen and excess nitric acid, diluted to a known volume, and the phosphorus was determined by the usual ammonium molybdate precipitation method.

Table III lists the experimental values obtained for several determinations by this technique. It is apparent that factors such as length of precipitation, severity of agitation, and amount of washing of the precipitate are very critical when this oxidation is employed. It was further found that P - C links were cleaved satisfactorily by this oxidation but difficulty was encountered when nitrogen was linked to the phosphorus atom.

Sulfuric Acid-Hydrogen Peroxide Method.--It is reported by Niederl (129) that satisfactory phosphorus analyses of organophosphorus compounds can be obtained utilizing sulphuric acid-hydrogen peroxide oxidation followed by molybdate precipitation. The work was done on a micro scale and required that the molybdate precipitate be boiled with excess sodium hydroxide to remove all the ammonia from the solution. This required the use of a P/28,000 factor as derived from the equation

Table 3. Analysis of Phosphorus Compounds by the HNO_3-$KMnO_4$ Technique

Compound	Procedure	Oxidation Time (hrs.)	Precipitation Time (hrs.)	Analysis (% P)	Theoretical (% P)
$PhP(O)(NH_2)_2$	Add $KMnO_4$ until prec. just forms	4	0.5	16.38	19.88
$PhP(O)(NH_2)_2$	Wt. $KMnO_4$ equal to 8 times sample wt.	6	0.5	15.65	19.88
Same liquor as above	-----	-	0.5 with shaking	18.12	19.88
Same liquor as above	-----	-	3 with shaking	19.20	19.88
$PhP(O)(NH_2)_2$	Repeat analysis run as above	4	0.5	15.30	19.88
$PhP(O)(NH_2)_2$	Use 5% $KMnO_4$ until prec. remains	4	0.5	17.35	19.88
Same liquor as above	-----	-	24	17.50	19.88
$PhP(O)(NH_2)_2$	Repeat analysis run as above	4	0.5	17.05	19.88
Same liquor as above	-----	-	24	17.15	19.88
$PhP(O)(OH)_2$	Use 5% $KMnO_4$ until prec. remains	0.5	0.5	18.60	19.60
Same liquor as above	-----	-	24	19.50	19.60

$$(NH_4)_3PO_4\cdot 12MoO_3\cdot 2HNO_3 + 28\ NaOH \longrightarrow$$
$$12\ Na_2MoO_4 + 2\ NaNO_3 + Na_2HPO_4 + 16\ H_2O + 3\ NH_3.$$

The usual reported analysis using alkali titration recommends the use of the factor P/23,000 as derived from the equation

$$(NH_4)_3PO_4\cdot 12MoO_3 + 23\ NaOH \longrightarrow$$
$$11\ Na_2MoO_4 + Na(NH_4)HPO_4 + (NH_4)_2MoO_4 + 11\ H_2O.$$

This latter procedure recommends washing the ammonium phosphomolybdate precipitate with voluminous amounts of water in order to wash away not only the stray acid that may be occluded during the precipitation but also the 2 HNO_3 reportedly present in the procedure of Niederl.

The simplest and most rapid procedure possible would, therefore, not utilize excessive washing of the precipitate and would not attempt to boil out the ammonia by heating in the presence of excess alkali. If such a procedure did prove to be satisfactory, then the predicted factor would have to be P/25,000 as derived from the equation

$$(NH_4)_3PO_4\cdot 12MoO_3\cdot 2HNO_3 + 25\ NaOH \longrightarrow$$
$$11\ Na_2MoO_4 + Na(NH_4)HPO_4 + (NH_4)_2MoO_4 + 2\ NaNO_3 + 13\ H_2O.$$

The feasibility of using such a procedure was quite definitely verified. In all cases examined, it was found that excessive washing of the precipitate with 2 per cent sodium nitrate solution consistently lowered the phosphorus content. This could indicate that the large amount of washing recommended by the technique employing P/23,000 encourages low results because of possible solution of some of the precipitate. If small wash liquors were employed, it was found that high results were obtained by using the P/23,000 factor, but accurate values were obtained on the basis of the P/25,000 factor. It was further found that the time spent liberating NH_3 was spent unnecessarily, on the macro scale at least, since very good checks were obtained for the phosphorus content regardless of whether the NH_3 was liberated or not.

The method finally decided on for the determination of phosphorus utilized a sulphuric acid-hydrogen peroxide liquor to decompose the compound and to oxidize the phosphorus to the phosphate state followed by subsequent precipitation as ammonium phosphomolybdate. The precipitate was washed lightly with two per cent sodium nitrate and titrated with standard alkali using P/25,000 as the factor. An accurately weighed sample of about 0.10 g. was placed into a 50-ml. pyrex test tube and five glass boiling beads were added to eliminate splattering of the liquid during subsequent heating. Five milliliters of concentrated sulphuric acid was added and the tube heated to SO_3 fumes. After cooling, 10 ml. of 30 per cent hydrogen peroxide was added in a dropwise manner and heated until SO_3 fumes appeared. This oxidation step was then repeated and then 10 ml. of water was added and the liquor was again heated to SO_3 fumes. This latter step was included to insure any cleavage that may be facilitated by dilute rather than concentrated acid. The oxidation step was repeated using only 5 ml. of the 30 per cent peroxide. The liquor was then heated to SO_3 fumes twice using two separate 10-ml. portions of water in order to remove all of the excess peroxide. The solution was neutralized with ammonium hydroxide, made acidic with 3.0 ml. of concentrated nitric acid, and adjusted to

250 ml. total volume. A 25-ml. portion of this solution was then added to 75 ml. of water containing 15 g. of ammonium nitrate and 2 ml. of 1 per cent gelatin solution. This liquor was heated to 40° C. and 45 ml. of ammonium molybdate precipitating solution was added. The precipitating solution was prepared immediately before being used by adding 15 ml. of ammonium molybdate (made up by mixing 400 ml. of water and 80 ml. of concentrated ammonium hydroxide and dissolving 100 g. of ammonium molybdate in this liquor) to 30 ml. of nitric acid (made by mixing 400 ml. of concentrated nitric acid with 600 ml. of water). The flask was shaken intermittently for 30 minutes, and the precipitate was then suction-filtered through an asbestos matted gooch crucible prepared so as to have the thinnest asbestos matting possible. The precipitate was washed with 150 ml. of two per cent sodium nitrate, transferred quantitatively into the precipitating flask and titrated with standard alkali. The best end point was obtained by overtitrating the precipitate with excess alkali, adding excess standard hydrochloric acid, and finally titrating to a pink end point with alkali using phenophthalein indicator.

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