SYNTHESIS AND EVALUATION OF NEW DYESTUFFS FOR HYDROPHOBIC FIBERS

A THESIS

Presented to
the Faculty of the Graduate Division

by
Samuel Michael Hong

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of the Requirements for the Degree
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SYNTHESIS AND EVALUATION OF NEW DYESHUFFS

FOR HYDROPHOBIC FIBERS

Approved:

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DEDICATION

TO MY MOTHER AND FATHER
ACKNOWLEDGMENTS

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ABSTRACT

Attempts were made to synthesize phosphorus-containing azo dyestuffs which could be applied directly to hydrophobic synthetic fibers without the use of either chemical dyeing assistants or temperatures above the boil.

Four phosphorus-containing intermediates — phenyl-dianilidophosphonamidate, tricresyl phosphate, triphenyl phosphate, and o-chlorophenyl-di phenyl phosphate — were used as coupling components. The diazonium salts used were obtained from 2,4-dinitroaniline, p-nitroaniline, 2,5-dichloroaniline, 4-chloro-2-nitroaniline, and o-aminoazotoluene.

A colored compound, believed to be a mixture of 2,4-dinitroaniline and a small amount of a reddish-brown phosphorus-containing product, and capable of dyeing nylon, Dacron, Darlan, acetate, Orlon, Dynel, and Acrilan, was obtained in small yield from the reaction of diazotized 2,4-dinitroaniline and phenyl-dianilidophosphonamidate. The chemical identity of the phosphorus-containing portion of this mixture was not determined.

The wash- and lightfastness properties of this product, when applied to Dacron, Darlan, acetate, and Orlon, are very satisfactory. Of particular interest, however, is the fact that this colored compound has the ability to dye
these fibers at the boil from an aqueous solution; the addition of no other reagents to the dyebath is required.

Colored compounds with dyeing properties were also obtained from reactions between phenyldianilidophosphonamidate and 2,5-dichloroaniline or p-nitroaniline; triphenyl phosphate or o-chlorophenyldiphenyl phosphate and diazotized 2,4-dinitroaniline.

In two unsuccessful experiments, attempts were made to condense 2,4-dinitro-4'-aminoazobenzene with dichlorophenylphosphine oxide.
CHAPTER I

INTRODUCTION

The introduction, in the early nineteen hundreds, of cellulose acetate fibers on a commercial scale presented serious problems to the dyer. The dyestuffs available at that time could not successfully be applied to this new fiber. Consequently, a frantic search for dyes for cellulose acetate began; this problem was solved in 1923 by the development of a new class of dyestuffs which were water insoluble and could be applied directly to the fiber from a fine aqueous suspension (1). Development of these colors was effected by a trial and error method; information concerning the mechanism of dyeing was limited.

Today a similar situation exists. There are several new fibers, some introduced since 1950, which also present serious dyeing problems. These problems have been circumvented by "forcing" the existing dyestuffs into these new fibers, either by the use of chemical assistants such as swelling agents and "carriers" or by the use of high temperature (generally up to 250°F.) and pressure.

The present-day situation differs from that which existed in the early nineteen hundreds in that there is now a much better understanding of the mechanism of dyeing, including
information about fiber structure and structural requirements of dyestuffs for specific fibers. Also, within the past thirty years, an increasing number of new products has been discovered and manufactured to give those concerned a wider range of material with which to work.

To meet the challenge of the dyeing problems that are presented by some of the recently developed synthetic fibers and to investigate the possibilities of certain new complex materials which possess interesting properties that might prove useful as dyestuff intermediates, syntheses of new dyes were attempted.

Organophosphorus compounds were chosen for this work with particular attention to those containing the P—O group.

The application of organophosphorus compounds to the textile field up to this time has been relatively limited, particularly in the dyestuff industry. In 1936 Hall (2) reported that certain complex compounds of phosphorus had been useful as textile assistants, such as for improving direct dyeing and in vat dyeing of cellulose fibers. He related that by replacing the hydrogen atoms of phosphine with organic radicals and by further treatment with alkyl halides (methyl and ethyl bromides) it is possible to form compounds in which the phosphorus is pentavalent. These resemble the basic quaternary ammonium compounds and are useful as textile assistants. The addition of these phosphonium compounds (which contain at least one aliphatic
or aromatic residue having not less than six carbon atoms) to the dyebath make it possible to secure better penetration of the textile material and more level dyeing. Suitable compounds of this type are trimethyl-octyl-phosphonium hydroxide and triethyl-cetyl-phosphonium bromide.

Rossin (3), in 1956, observed that deep shades can be obtained, when dyeing acrylonitrile homo- or copolymers with direct cotton dyes, with the aid of certain water-soluble benzyltris-(diakylamino)-phosphonium compounds as assistants. These assistants were added either directly to the dyebath or by preparing the fiber with these compounds before dyeing.

Kosolapoff and Priest (4) used phosphonic acid residues in place of sulfonic acids in the synthesis of materials that have dye properties. The substances selected for study were methyl orange, ethyl orange, and congo red. These workers found that the phosphonic acid analogs of methyl orange and ethyl orange showed almost no affinity for cotton fabrics, but were readily applied, with good leveling properties, to silk and wool. The phosphonic acid analog of congo red was found to be an excellent direct dye, for cotton, silk, and wool. All dyes that showed affinity for the various fabrics showed excellent fastness without evidence of fading or running.
Phenyldianilidophosphonamidate

Preparation of Phenyldianilidophosphonamidate \((C_6H_5NH)\_2P(O)C_6H_5\)

The method of preparation used for this compound was essentially that described by Michealis (5) and involved the reaction of phenyldichlorophosphine oxide with excess aniline. Phenyldichlorophosphine oxide (Eastman Yellow Label, used without further purification), 185 g. (1.0 mole), was added in a dropwise manner with stirring to 465 g. (5.0 mole) of aniline (C.P.). The temperature of the mixture was kept below 5° C. by external cooling. After the addition was complete, the mixture was filtered to remove the solid product. The phenyldianilidophosphonamidate, after recrystallization from hot methanol, was obtained as white flakes, which melted at 214° C.* The reported melting point for this product is 213° C.(5).

Diazotization of 2,4-dinitroaniline

Method 1.--Sodium nitrite (Technical Crystals), 3.5 g. (0.05 mole), was slowly added with stirring to sulfuric acid (C.P.) (75 ml, sp. gr. 1.80). The temperature of the nitrosylsulfuric

*All melting points were run with the same uncalibrated thermometer.
acid solution was allowed to rise to 40° C. Next 9.15 g. (0.05 mole) of 2,4-dinitroaniline (Eastman Red Label) was added slowly, and the temperature was kept between 30 and 35° C. during the addition. The mixture was stirred mechanically at room temperature for 2 hours. When a test drop with water showed only a slight precipitate of base, the mixture was poured on ice, allowed to stand until the insoluble impurities settled, then filtered and diluted with water to 450 ml. (6).

Method 2.—26.4 ml. of sulfuric acid (Baker's Reagent) was cooled in an ice bath, and to this 4.2 g. of sodium nitrite (Technical Crystals) was gradually added with stirring. The temperature of the mixture was kept below 10° C. Stirring was continued for 10 minutes after the nitrite had been added, and then the mixture was transferred to a water bath at room temperature. When the temperature of the mixture had reached that of the water bath, very gradual heating was started and continued until the temperature reached 70° C. The mixture was then stirred at this temperature until all the nitrite had dissolved. When a clear solution was obtained, it was cooled on ice to 20° C. (bisulfate separated), and 10.98 g. (0.06 mole) of pulverized 2,4-dinitroaniline was added in small portions. The mixture was stirred at room temperature until a test sample, diluted with ice water, gave only a faint test for nitrite. The reaction mixture was then
poured on to 144 g. of ice, and the resulting solution was filtered to remove small amounts of undissolved material. The diazo solution was used without delay (7).

Method 3.—The diazotization procedure described by Saunders (6) was followed with the exception that ice was omitted and less sulfuric acid was used. Sodium nitrite (2.8 g.; 0.04 mole) was slowly added in small quantities to 18 ml. of concentrated sulfuric acid. During the addition the temperature was allowed to rise to 40°C. The solution was stirred until the nitrite had been completely dissolved. Into this solution, pulverized 2,4-dinitroaniline (7.3 g.; 0.04 mole) was slowly added at 30-35°C. The mixture was stirred at room temperature for 2 hours, then allowed to stand until insoluble impurities settled. The insoluble product was removed by filtration, and the clear solution was used immediately.

Method 4.—3.0 g. (0.0435 mole) of sodium nitrite was added to a solution of 30 ml. of concentrated sulfuric acid and 15 ml. of water which had been cooled to 10°C. To this, 3.66 g. (0.02 mole) of 2,4-dinitroaniline dissolved in 15 ml. of pyridine (Eastman Yellow Label) was slowly added with constant stirring. The temperature was kept below 10°C. during this addition. The solution was stirred for 30 minutes after addition of the 2,4-dinitroaniline was complete. Twice the volume of ice water was then added. Finally 2 g. of urea was
introduced with stirring to remove excess nitrous acid, and stirring was continued until foaming had ceased. The slight residue which resulted on the addition of urea was removed by filtration (8).

Method 5.—The diazonium salt solution was prepared as outlined in Method 4 with the exception that the addition of ice water was omitted.

Reaction of Phenyldianilidophosphonamidate with Diazotized 2,4-dinitroaniline

Experiment 1.—3.1 g. (0.01 mole) of phenyldianilidophosphonamidate was dissolved, with the aid of heat, in 50 ml. of glacial acetic acid (Baker's Reagent). To the mixture, 2 g. of sodium acetate (Baker's Reagent) was added. The whole was mechanically stirred until the solution was clear, then cooled to room temperature in an ice bath. Then 90 ml. (0.01 mole) of 2,4-dinitroaniline, diazotized by Method 1, was added in small quantities to the above mechanically stirred acid solution of phenyldianilidophosphonamidate. When the solution (Sample 1) was completely clear, 10 ml. of the mixture was diluted to twice its volume with water. An orange-colored precipitate formed which dissolved almost completely when the solution was heated to the boil. To this boiling solution Dacron fibers were added and stirred for 10 minutes, washed, and air dried. The sample was uniformly
dyed a bright orange color. The above dyeing procedure was repeated with an array of synthetic fibers and the following results were obtained: nylon was dyed a reddish brown; Orlon, yellowish brown; Acrilan and Dynel, brown; and acetate, reddish orange.

Sample 1, upon standing in the dark and at room temperature for one day, acquired a dark red color. 10 ml. of this solution was prepared for dyeing a sample of Dacron fiber in the same manner as described above. The result of this treatment yielded a uniformly dyed orange sample which was darker than the above dyed Dacron.

Sample 1 was filtered by suction and a charcoal colored crystalline material (Sample 2) and a dark red filtrate (Sample 3) were obtained. Sample 2 was mixed with approximately 400 ml. of water and heated to the boil. Although the solid was only slightly soluble to give a pale yellow solution, a thin layer of red liquor separated at the surface. This two-phase system dyed a sample of Dacron fibers a uniform orange color at the boil.

To the mechanically stirred Sample 3, three times its volume of water was added. After the mixture had been stirred for 30 minutes, it was filtered. The pale yellow acetic acid filtrate obtained was discarded. Approximately 400 ml. of water was added to the reddish black residue, and the mixture was heated to the boil for 30 minutes before filtering by suction. The water insoluble black crystalline residue
(Sample 4) weighed about 0.1 g. The red filtrate (Sample 5) obtained was extracted with one half its volume of ether (U.S.P.) and the ether extract was allowed to evaporate at room temperature. The dry product, which was a dark red crystalline material, was recrystallized from hot water to give approximately 0.5 g. of a sample that melted at 174-176°C. This sample, when dissolved in hot water, dyed nylon, Dacron, and acetate fibers at the boil.

Experiment 2.—3.1 g. (0.01 mole) of phenyldianilidophosphonamidate and 25 g. of sodium acetate were dissolved in 100 ml. of hot glacial acetic acid. After cooling to room temperature, 1.83 g. (0.01 mole) of 2,4-dinitroaniline, diazotized as described in Method 2, was slowly added with stirring. The mixture was allowed to stand at room temperature over a period of one hour, then filtered by suction. The product obtained (10.2 g.) consisted essentially of sodium acetate, contaminated with a very small amount of brown crystalline material.

Experiment 3.—3.1 g. (0.01 mole) of phenyldianilidophosphonamidate was dissolved, by heating, in 100 ml. of glacial acetic acid, then cooled to room temperature in an ice bath. To this, 1.83 g. (0.01 mole) of 2,4-dinitroaniline diazotized as described in Method 2, was added with vigorous stirring. Stirring was continued until solution was complete. After 2 hours in the dark and at room temperature, the mixture, orange in color, was filtered by suction to yield a reddish-orange crystalline residue. The solid was pulverized and
mixed with 400 ml. of water, heated at the boil for 30 minutes, then filtered to remove the water insoluble product. The red filtrate obtained was heated to the boil; to this, various samples of synthetic fibers were added and treated with agitation for 10 minutes, rinsed, and air dried. Nylon was dyed brown; Orlon, light-brown; acetate and Dacron, orange.

Experiment 4.—18.5 g. (0.06 mole) of phenyldianilidophosphonamidate was added with stirring to 650 ml. of glacial acetic acid. To this 22 g. (0.12 mole) of 2,4-dinitroaniline, diazotized as described in Method 1, was added slowly with mechanical stirring. Stirring was continued for 30 minutes after the diazotized base had been added. A dark red solution, which had a pH of 2, was obtained. The reaction mixture was mechanically stirred while water, equal to 50 times its volume, was gradually added. The brown crystalline precipitate which separated from solution was isolated by filtration, then dried at 55°C. for 2 hours. This mass was ground in a mortar, in small portions, with ether; and the red-colored ether solution was decanted from the insoluble material. A total of 250 ml. of ether was used. The combined ether extracts were evaporated to dryness on a hot water bath to yield a reddish-brown residue. This solid was pulverized, mixed with 1 liter of water, heated at the boil for 1 hour, then filtered. The filtrate was cooled in an ice bath for 6 hours, then filtered to yield 1.5 g. of reddish-brown crystalline material that melted at 166-168°C. Recrystal-
lization from approximately 500 ml. of hot water raised the melting point to 171-175°C. A second recrystallization from approximately 400 ml. of hot water yielded a product which melted at 173-176°C. The final compound, which was in the form of reddish-brown crystals, was used to dye a series of synthetic fibers, the wash- and lightfastness properties of which were determined. (See Analytical and Testing Procedures.)

Experiment 5.—3.1 g. (0.01 mole) of phenyldianilidophosphonamidate was dissolved, with the aid of heat, in 250 ml. of glacial acetic acid. After cooling to 20°C. in an ice bath, 3.66 g. (0.02 mole) of 2,4-dinitroaniline, diazotized as outlined in Method 3, was gradually added in small quantities. When the addition was completed, the reaction mixture was a dark red in color (Sample 1), and had a pH of 1.

Next, 10 ml. of the mixture was added to twice its volume of water and heated to the boil. To this solution a sample of Dacron fiber was entered, treated for 5 minutes with intermittent agitation, washed, rinsed, and then air dried. The resultant sample was uniformly dyed an orange color. The above dyeing procedure was repeated on samples of other synthetic fibers; it was observed that nylon was dyed reddish-brown; acetate, bright red; Dynel and Acrilan, dull red; and Orlon, light-brown. Some fiber degradation was noticed during these dyeing treatments.
After one day of standing, in the dark and at room temperature, Sample 1 became slightly darker in color. A sample of Dacron fiber was dyed in 10 ml. of this mixture, prepared for dyeing as described above; a noticeably darker shade of orange was obtained on this sample as compared with the first dyed sample of Dacron.

The remainder of Sample 1 was filtered to remove the small amount of solid material present. The filtrate was heated at the boil for 30 minutes, then allowed to stand for two days in the dark and at room temperature. The mixture was extracted with approximately 75 ml. of ether; then the ether extract was evaporated to dryness on a water bath to yield a blackish brown crystalline material. The solid, after recrystallization from hot water, gave a poor yield (approximately 0.2 g.) of brick brown crystals. An aqueous solution of this product, heated at the boil and without the aid of assistants, was able to dye Dacron, nylon, and acetate fibers directly.

Experiment 6.—30.8 g. (0.1 mole) of phenyldianilidophosphonamide, dissolved in 650 ml. of glacial acetic acid, was cooled to 20-25°C. in an ice bath; 36.6 g. (0.2 mole) of 2,4-dinitroaniline, diazotized according to the procedure outlined in Method 2, was slowly added with stirring. To this, 1800 ml. of water was gradually added with mechanical agitation, and stirring was continued at room temperature
for 4 hours. During the stirring operation, a precipitate separated as tarry particles which eventually coagulated into a black mass. This solid was removed by filtration. The aqueous filtrate was extracted with a volume of ether equal to one-half the volume of the aqueous solution, and the ether extract was evaporated to dryness on a water bath. The residue, after recrystallization from approximately one l. of water, melted at 175-178°C.; a second recrystallization from approximately 800 ml. of hot water raised the melting point to 177-179°C.; a third recrystallization from approximately 600 ml. of hot water yielded a product which melted at 178-179°C.; and a fourth recrystallization from approximately 400 ml. of water gave a product which melted sharply at 179°C. The resulting reddish-brown crystalline material, which weighed approximately 1.2 g., was sent out to the Clark Microanalytical Laboratory for analysis. The reported results were as follows:

Carbon 39.41 and 39.52%, ave. 39.46%
Hydrogen 2.74 and 2.57%, ave. 2.63%
Nitrogen 22.39 and 22.60%, ave. 22.50%
Oxygen (by difference) 35.41%

(Calculated percentages for 2,4-dinitroaniline are: C, 39.34%; H, 2.73%; N, 22.95%; and O, 34.97%.)

Phosphorus determinations, made by the Method described in the Analytical and Test Procedures Section, indicated the presence of 1.15 per cent and 1.03 per cent of phosphorus.
A mixed melting point of this product with 2,4-dinitroaniline melted at 179°C. This product, like that obtained in Experiment 5, satisfactorily dyed Dacron, nylon, acetate, Dynel, Acrilan, Orlon, and Darlan fibers at the boil in an aqueous solution.

Experiment 7.—0.915 g. (0.005 mole) 2,4-dinitroaniline, diazotized as described in Method 4, was introduced with stirring into 1.54 g. (0.005 mole) of phenyldianilidophosphonamidate dissolved in 20 ml. of glacial acetic acid. A dark red solution was obtained which had a pH of 1. This solution was allowed to stand in the dark at room temperature for two days, then added to twice its volume of water and stirred for one hour. The brown crystals which separated were isolated by filtration. After pulverizing the material, it was added to approximately 200 ml. of water, and heated to the boil for 15 minutes; filtered to remove undissolved particles, then again heated to the boil. The solution was used at the boil to attempt dyeing synthetic fibers. Dacron was dyed orange; nylon, red; acetate, orange-yellow; and Orlon, pale yellow.

Experiment 8.—0.915 g. (0.005 mole) of 2,4-dinitroaniline, diazotized as described in Method 4, was slowly added with stirring to 1.54 g. (0.005 mole) of phenyldianilidophosphonamidate dissolved in 80 ml. of pyridine. During the addition the mixture reacted violently, generating considerable
heat and foam; a precipitate separated immediately. After the reaction subsided, the mixture was filtered; a dark red filtrate and a yellowish-brown residue were obtained.

Experiment 9.—0.915 g. (0.005 mole) of 2,4-dinitroaniline, diazotized as outlined in Method 5, was introduced with stirring to 1.54 g. (0.005 mole) of phenyldianilidophosphonamidate dissolved in 20 ml. of glacial acetic acid. The mixture formed had a dark red color with a pH of 1. This solution was allowed to stand in the dark and at room temperature for one day. Twice its volume of water was then added with stirring. The solid material which separated was removed by filtration, then dried at 55°C. for 2 hours to yield 0.32 g. of a reddish-black material. This solid was pulverized before adding to approximately 400 ml. of water; heated at the boil for 30 minutes and filtered. The red filtrate was cooled in an ice bath for one day, and the solid, which came out of solution, was removed by suction filtration. The residue was dried at 55°C. for 2 hours. This residue was in the form of reddish-brown crystals which weighed approximately 0.2 g. Nylon was dyed red in a hot aqueous solution of this product.

Experiment 10.—0.915 g. (0.005 mole) of 2,4-dinitroaniline, diazotized as described in Method 5, was slowly introduced with stirring to 1.54 g. (0.005 mole) of phenyldianilidophosphonamidate dissolved in 80 ml. of pyridine. During the addition, solid material gradually formed and considerable
heat was evolved. After the reaction had subsided to the extent where foaming had ceased, the mixture was diluted with twice its volume of water. The mixture was then filtered to yield a light brown residue and a dark red filtrate.

Experiment 11.—3.66 g. (0.02 mole) of 2,4-dinitroaniline, diazotized as outlined in Method 4, was reacted with 3.08 g. (0.01 mole) of phenyldianilidophosphonamidate dissolved in 75 ml. of glacial acetic acid. The mixture obtained was allowed to stand 14 hours at room temperature before diluting with twice its volume of water, then stirred for 2 hours. A brown precipitate separated. The mixture was filtered to yield a red residue (Sample 1) and a dark reddish-brown filtrate (Sample 2). Sample 2 was extracted with ether, the ether extract was evaporated to dryness on a water bath. The residue was added to benzene, heated to the boil, boiled for 5 minutes, then suction filtered. The benzene insoluble residue was in the form of black crystals which were also insoluble in ethyl alcohol and hot water but readily soluble in dioxane (Practical). The red dioxane solution did not dye synthetic fibers.

The benzene filtrate was evaporated to dryness on a water bath and the dry solid was pulverized and mixed with approximately 300 ml. of water and boiled for 30 minutes before filtering. The pale red filtrate was discarded. The residue was a black crystalline material that was insoluble in hot water.
Experiment 12.---3.66 (0.02 mole) of 2,4-dinitroaniline, diazotized as described in Method 5, was slowly added with stirring to 3.08 g. (0.01 mole) of phenyldianilidophosphonamide dissolved in 75 ml. of glacial acetic acid. The mixture was allowed to stand at room temperature for 14 hours. Twice its volume of water was added with stirring, then the mixture was filtered to yield approximately 0.5 g. of a black tarry solid (Sample 1). Sample 1 was insoluble in hot water; slightly soluble in benzene. The benzene solution formed a pale yellow solution with a red surface film.

The filtrate from Sample 1 was extracted with ether and the red ether solution was evaporated to dryness on a water bath. The dark reddish-brown residue was boiled with 500 ml. of water for 20 minutes. Solution of the residue was not complete. The mixture was filtered to give a dark red filtrate (Sample 3) and a brick brown crystalline material (Sample 2) which melted at 182-184°C.

The hot water insoluble residue (Sample 2) was partially soluble in benzene. The red colored benzene solution was filtered to yield a reddish-brown residue (Sample 4) which melted at 188-190°C., and a red filtrate. The benzene was evaporated from the filtrate with the aid of a water bath. The residue (Sample 5) obtained was in the form of brown crystals which melted at 166-168°C. and dissolved readily in hot water to give a red solution. (Note that this product came from the water insoluble Sample 2.)
This solution dyed nylon, Dacron, and acetate fibers at the boil. The per cent phosphorus in this product was determined as described in the section on Analytical and Testing Procedures and was found to be 1.8 per cent.

Sample 3 was cooled on ice for one day and filtered. The filtrate was discarded. The residue (Sample 6), which was brick brown in color, melted at 163-165°C; a mixture of Samples 5 and 6 melted at 138-140°C. It was partially soluble in hot water to form a red solution, which dyed Dacron fibers orange. The hot water insoluble fraction of Sample 6 (Sample 7) melted at 175-176°C. The filtrate (Sample 8) was a red colored liquor which dyed nylon fibers brown at the boil. The colored product in Sample 8 was extracted with benzene. The benzene solution was evaporated on a water bath to dryness. A brick brown solid was obtained which melted at 123-127°C.

Sample 7, which was insoluble in hot water, was a brown colored mass. This solid was added to benzene and stirred for 10 minutes before filtering. The residue obtained was in the form of yellowish orange crystals which melted at 176-177°C. The filtrate obtained was evaporated to dryness on a water bath. The resulting product (Sample 9) melted at 155-156°C. An aqueous solution of the product, heated to the boil, dyed Dacron, nylon, acetate, and Darlan fibers.
Reaction of Tricresyl Phosphate \((\text{CH}_3\text{C}_6\text{H}_{4}\text{O})_3\text{P}(\text{O})\) with Diazotized 2,4-Dinitroaniline.

**Experiment 1.**—3.7 g. (0.01 mole) of tricresyl phosphate (Fisher Technical; 80% Para, 20% Meta) was dissolved in 100 ml. of glacial acetic acid mixed with 25 g. of sodium acetate. Into this solution, 28.4 ml. (0.01 mole) of a solution of diazotized 2,4-dinitroaniline, diazotized as outlined in Method 2, was slowly added with stirring at room temperature. The mixture, which acquired a yellowish orange color and had a pH of 6, was allowed to stand in the dark at room temperature for 1 hour, then filtered by suction to yield approximately 9 g. of a brown crystalline material. 0.5 g. of the solid was suspended in approximately 100 ml. of water, then brought into solution by heating the mixture to the boil; an oily brown solution resulted. A sample of nylon fiber, treated for 5 minutes at the boil in this solution, then rinsed and air dried, acquired a light brown tint.

**Experiment 2.**—50.0 g. of sodium acetate was slowly added with stirring to 3.7 g. (0.01 mole) of tricresyl phosphate dissolved in 100 ml. of glacial acetic acid. To this solution, 3.66 g. (0.02 mole) of 2,4-dinitroaniline, diazotized as described in Method 2, was added slowly with stirring. When the addition was completed, the mixture was allowed to stand in the dark and at room temperature for 2 hours, at which time the mixture, a reddish-brown color with a pH of 2.5, was filtered to yield a brown solid. The solid was added to
approximately 250 ml. of water, then heated to the boil; into
this was entered a sample of Dacron fiber, which was boiled
for 10 minutes with intermittent agitation, rinsed, and air
dried. The sample was unevenly dyed a brown color.

Experiment 3.--2.0 g. of sodium acetate was slowly added
with stirring to 3.68 g. (0.01 mole) of tricresyl phosphate
dissolved in 25 ml. of glacial acetic acid. To this, 0.009 mole
of 2,4-dinitroaniline, diazotized as described in Method 1,
was added and mechanically stirred for 30 minutes. 10 ml. of
the oily yellow mixture was added to twice its volume of
water, then heated to the boil. A sample of Dacron fiber
was introduced into the boiling solution and treated with
agitation for 10 minutes, rinsed with cold water, and air
dried. The sample was slightly tinted a yellowish color.

Reaction of Triphenylphosphite \((\text{C}_6\text{H}_5\text{O})_3\text{P}\) with Diazotized
2,4-dinitroaniline.

3.1 g. (0.01 mole) of triphenylphosphite was dissolved
in 100 ml. of glacial acetic acid mixed with 25 g. of sodium
acetate. To this, 28.4 ml. (0.01 mole) of 2,4-dinitroaniline,
diazotized as described in Method 2, was slowly added with
stirring. The mixture was allowed to stand in the dark at
room temperature for 1 hour, then suction filtered. The
filtrate, a red colored solution with a pH of 5, was heated
at the boil for 30 minutes, then left in the dark at room
temperature for one day. The mixture was filtered and air
dried to yield a yellowish orange mass (Sample 1) that
weighed 3.6 g.
0.5 g. of Sample 1 was mixed with approximately 150 ml. of water and heated at the boil for 20 minutes; this yielded an oily red solution containing a small amount of insoluble material which was removed by filtration. Samples of synthetic fibers were treated at the boil for 10 minutes in the red filtrate obtained, rinsed, and air dried. Nylon was dyed olive green; acetate and Dynel, yellow; Orlon, Dacron, and Acrilan, light brown.

0.5 g. of Sample 1 was added to 100 ml. of 3% sulphuric acid and boiled for 15 minutes, then cooled to room temperature with the aid of an ice bath. The solution was extracted with 30 ml. of carbon tetrachloride (Reagent). The carbon tetrachloride solution was evaporated to dryness on a water bath to yield a pale orange-brown residue. The solid was mixed with 75 ml. of water and heated at the boil for 15 minutes, filtered hot and again heated at the boil. To this hot yellow solution, samples of nylon and Orlon fibers were treated for 10 minutes, rinsed, and air dried. It was observed that the nylon sample was dyed a pale green and the Orlon sample was not colored.

Reaction of o-Chlorophenyldiphenyl Phosphate (ClC₆H₄O)(C₆H₅O)₂P(O) with Diazotized 2,4-Dinitroaniline.

Experiment 1.—3.61 g. (0.01 mole) of o-chlorophenyldiphenyl phosphate (Eastman Yellow Label) was dissolved in 200 ml. of glacial acetic acid mixed with 100 g. of sodium acetate. To this, 90 ml. (0.01 mole) of a solution of 2,4-dinitroaniline,
diazotized as outlined in Method 1, was introduced slowly with stirring. The mixture, which formed an orange-colored solution with a pH of 3.5, was filtered and air dried to yield 35 g. of a light gray crystalline material. The solid was soluble in hot water to form a brown solution which had little or no affinity for textile fibers.

Experiment 2.—1.83 g. (0.01 mole) of 2,4-dinitroaniline, diazotized as outlined in Method 2, was introduced slowly with stirring to 3.6 g. (0.01 mole) of o-chlorophenyl-diphenyl phosphate dissolved in 100 ml. of glacial acetic acid. The mixture formed a reddish orange solution which had a pH of 1. To this solution, an equal volume of water was gradually added with stirring. Stirring was continued for 1 hour before filtering to yield a pale red solid. A small portion of this solid, in boiling water, did not dye Dacron or Orlon fibers.

Experiment 3.—50.0 g. of sodium acetate was introduced with stirring to 3.6 g. (0.01 mole) of o-chlorophenyl-diphenyl phosphate dissolved in 100 ml. of glacial acetic acid. To this, 56.8 ml. (0.02 mole) of diazotized 2,4-dinitroaniline, diazotized as described in Method 2, was added in small portions with stirring at room temperature. The mixture, which had a pH of 5, was then filtered. The red filtrate obtained was boiled for 30 minutes, then allowed to cool in the dark at room temperature for one day. Filtration yield approximately 20.0 g. of a brown crystalline material which was found to be soluble in hot water. This solution imparted a
brown color to nylon, Orlon, and Dacron fibers at the boil. However, considerable degradation to the fibers also occurred. The solid was recrystallizable from methyl alcohol.

Reaction of Phenylidianilidophosphonamidate with Fast Salts. Experiment 1.—0.77 g. (0.0025 mole) of phenylidianilidophosphonamidate was dissolved in 58.0 ml. of glacial acetic acid. To this, 3.24 g. of Fast Scarlet GG Salt (diazotized and stabilized 2,5-dichloroaniline; the 3.24 g. of commercial product used was assumed to represent 0.005 mole of 2,5-dichloroaniline) dissolved in 240 ml. of glacial acetic acid was added slowly with stirring. After the addition was complete, the mixture was allowed to stand in the dark and at room temperature for one day. Sodium acetate was then added, slowly and in small quantities, to the mixture until a pH of 5 was obtained, and the mixture again was allowed to stand in the dark and at room temperature for one day. Finally, 200 ml. of water was introduced slowly and with stirring to the mixture, at which time a precipitate separated gradually from solution. The mixture was stirred until precipitation had ceased and the solid was removed by suction filtration. The residue, in the form of brown crystals, was found to be insoluble in hot water but readily soluble in 95% ethanol. The ethanol solution was heated to the boil, and to this solution a sample of nylon fiber was entered and treated for 5 minutes, washed, and air dried. The sample was dyed a red color.
Experiment 2.—0.77 g (0.0025 mole) of phenyldianilidophosphonamidate was dissolved in 58.0 ml. of glacial acetic acid. To this, 2.15 g. of Fast Red 3GL Salt (diazotized and stabilized 4-chloro-2-nitroaniline; the 2.15 g. of stabilized diazonium salt was assumed to represent 0.005 mole of 4-chloro-2-nitroaniline) dissolved in 250 ml. of glacial acetic acid was gradually added. After standing for one day, in the dark and at room temperature, sodium acetate was added in small portions to raise the mixture to a pH of 5. After standing in the dark and at room temperature for another day, 200 ml. of water was slowly added to the mixture, then stirred for 30 minutes at room temperature before filtering. A brown crystalline material was obtained which was found to be insoluble in hot water but soluble in ethyl alcohol.

Experiment 3.—5.625 g. of Fast Garnet GB Salt (diazotized and stabilized o-aminoazotoluene; the 5.625 g. of commercial product was assumed to represent 0.005 mole of o-aminoazotoluene) dissolved in 240 ml. of glacial acetic acid was added slowly to 0.77 g. (0.005 mole) of phenyldianilidophosphonamidate dissolved in 58.0 ml. of glacial acetic acid. The mixture was allowed to stand in the dark and at room temperature for one day; sodium acetate was added until a pH of 5 was obtained. After standing in the dark at room temperature for a second day, 200 ml. of water was introduced with stirring. The mixture was stirred for 30 minutes, filtered, and the residue obtained yielded a mixture of
products, one light brown and the other white. The brown solid was found to be insoluble in either hot water or ethyl alcohol. The fine white flakes were soluble in ethyl alcohol.

Reaction of Phenylidianilidophosphonamidate with Diazotized p-Nitroaniline.

Experiment 1.—1.4 g. of sodium nitrite was added slowly with stirring to 20 cc. of concentrated sulphuric acid; the temperature was allowed to rise to 40°C. When the solution was complete, it was cooled to 0°C. in an ice bath. To the cold solution, 2.8 g. (0.02 mole) of p-nitroaniline, dissolved in 50 ml. of glacial acetic acid, was slowly added with stirring while the temperature was kept below 10°C. The mixture was stirred until clear, then allowed to stand for 10 minutes before 3.1 g. (0.01 mole) of phenylidianilidophosphonamidate dissolved in 152 ml. of glacial acetic acid was introduced slowly with stirring. The whole was stirred for 5 minutes before heating to the boil for 10 minutes, followed by the slow addition of an equal volume of water. The light red solution was extracted with ether. Evaporation of the ether extract to dryness yielded approximately 0.1 g. of a blackish-brown product, which was partially soluble in hot water. The water solution of this product dyed Dacron a pale yellow color at the boil.
Attempts to Condense 2,4-Dinitro-4'-Aminoazobenzene with Phenylidichlorophosphine Oxide C₆H₅P(O)Cl₂.

Experiment 1.—To 250 ml. of chloroform (CP) in a 500 ml. round bottom three neck flask was added 2.87 (0.01 mole) of 2,4-dinitro-4'-aminoazobenzene (a laboratory-prepared sample furnished by Ciba Co., Inc.) and 0.5 g. (0.0025 mole) of phenylidichlorophosphine oxide. The flask was fitted with a reflux condenser topped with a calcium chloride drying tube. The reaction mixture was refluxed for 26 hours, then cooled to room temperature and filtered to give a reddish-brown residue (Sample 1) which melted at 168-172°C.; a mixture of this solid with 2,4-dinitro-4'-aminoazobenzene (melting point 186-188°C.) melted at 170-172°C. A hot water solution of the product dyed Dacron and nylon fibers. The filtrate (Sample 2) obtained was a reddish-brown solution.

Sample 1 was mixed with 500 ml. of water, boiled for 1 hour, and filtered hot to yield a dark brown residue which melted at 175-177°C.; when mixed with 2,4-dinitro-4'-aminoazobenzene the mixture melted at 182-183°C. The pale yellow filtrate from Sample 1 was discarded.

Sample 2 was evaporated under pressure with slight heating to yield a brown crystalline material which was pulverized and mixed with 500 ml. of water, boiled for 30 minutes, and filtered hot to give a dark red residue (Sample 3) which melted at 189-191°C.; this solid, mixed with 2,4-dinitro-4'-aminoazobenzene, melted at 187-188°C. The red filtrate
(Sample 4) was cooled to room temperature and filtered. The solid obtained melted at 158-159°C. The pale yellow filtrate was discarded.

Experiment 2.—2.87 g. (0.01 mole) of 2,4-dinitro-4'-aminoazobenzene was placed in a 250 ml. round bottom three neck flask. To this, 0.975 g. (0.005 mole) of phenyldichlorophosphine oxide and 100 ml. of chloroform were added. The flask was set up with a reflux condenser topped with a calcium chloride drying tube. The mixture was heated to reflux, 35 cc. of pyridine was added in a drop-wide manner, and the mixture was refluxed for 46 hours. After cooling to room temperature the mixture was filtered to yield approximately 0.2 g. of a brownish-black crystalline material and a dark brown filtrate which was allowed to evaporate in the air.

The solid was recrystallized from 300 ml. of hot water to give a brick brown mass which melted at 190-192°C. The solid was again recrystallized from 300 ml. of hot water to yield approximately 0.1 g. of dark brown crystals which had a melting point of 195-197°C.

A mixed melting point of this product with 2,4-dinitro-4'-aminoazobenzene (M.P. 186-188°C.) resulted in a melting point of 189-192°C., and a mixed melting point with Sample 1 (M.P. 168-172°C.), of preceding Experiment 1, gave a melting point of 186-188°C.
Analytical and Testing Procedures

Determination of Phosphorus Content of Samples.—Turbak's (9) Sulphuric Acid-Hydrogen Peroxide Method was used for the determination of phosphorus. He reported that satisfactory phosphorus analysis of organophosphorus compound can be obtained utilizing sulphuric acid-hydrogen peroxide oxidation followed by molybdate precipitation. The method was outlined as follows: An accurately weighed sample of about 0.1 g. was placed in a 50 ml. pyrex test tube with five glass boiling beads. 5 ml. of concentrated sulphuric acid was added and the mixture was heated until SO₃ fumes were evolved. After cooling, 10 ml. of 30 per cent hydrogen peroxide was added in a dropwise manner, and the solution was again heated until SO₃ fumes appeared. This oxidation step was repeated, and then 10 ml. of water was added and the solution again heated until SO₃ fumes appeared. The oxidation step was repeated using 5.0 ml. of the 30 per cent peroxide. The solution was brought to SO₃ 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 added to 75 ml. of water containing 15 g. of ammonium nitrate and 2.0 ml. of one per cent gelatin solution. This solution was heated to 40°C., and 45 ml. of ammonium molybdate precipitating solution was added. The precipitating solution was made immediately before use by
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 solution) to 30 ml. of nitric acid (prepared by mixing 400 ml. of concentrated nitric acid with 600 ml. of water.) The mixture 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 minimum asbestos matting. The precipitate was washed with 150 ml. of a two per cent sodium nitrate solution, transferred quantitatively into the precipitating flask, and titrated with standard alkali to a phenolphthalein end point.

\[
\text{Per Cent Phosphorus} = \frac{P \ (\text{m.e. of base}) \times 100}{\frac{2500}{\text{wt. of sample}}} \frac{10}{10}
\]

Dyeing Procedures.—All samples were wet out in a two per cent solution of Nacconol NR (a sodium alkylarylsulfonate) solution for 15 minutes at 140-160°F, prior to dyeing. The dye was dissolved in water (50 ml. per gram of fiber to be dyed) by heating to the boil. No other additions to the dyebath were made. The fibers were entered at the boil, and dyeing was continued at that temperature, with intermittent stirring, for 45 minutes. The samples were removed from the dyebath, then scoured with a 2 per cent soda ash and 1 per cent soap solution at 160-180°F. for 15 minutes, rinsed with cold water, and air dried.
Colorfastness to Light.—Skeins of dyed yarn were tested for light-fastness according to the American Association of Textile Chemists and Colorists Standard Test Method 16A-54 (10), and evaluated on the basis of the number of clock hours required to effect just appreciable fading.

Colorfastness to Washing.—Number 3 washfastness tests were made according to the American Association of Textile Chemists and Colorists Standard Test Method 61-54 (11). The yarn to be tested was braided with undyed yarn of the same type. Evaluation of results was based on staining of the undyed yarn.
Table I. Fastness Properties of Phenylidianilidophosphonamidate and Diazotized 2,4-Dinitroaniline Reaction Product (Experiment 6) on Synthetic Fibers

<table>
<thead>
<tr>
<th>Fibers</th>
<th>Per Cent Dyeings (On Weight of Fibers)</th>
<th>Color Obtained</th>
<th>Light (Fade-Ometer) (^3) Hours to Cause Fading</th>
<th>Wash (Launder-Ometer) (^4) Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate(^1)</td>
<td>1</td>
<td>Orange</td>
<td>More than 40</td>
<td>5</td>
</tr>
<tr>
<td>Acrilan(^2)</td>
<td>1</td>
<td>Dull Orange</td>
<td>Approximately 5</td>
<td>5</td>
</tr>
<tr>
<td>Dacron(^2)</td>
<td>1</td>
<td>Orange</td>
<td>More than 40</td>
<td>5</td>
</tr>
<tr>
<td>Dynel(^1)</td>
<td>1</td>
<td>Dull Orange</td>
<td>Approximately 5</td>
<td>4-5</td>
</tr>
<tr>
<td>Nylon(^2)</td>
<td>1</td>
<td>Pale Red</td>
<td>Approximately 5</td>
<td>1-2</td>
</tr>
<tr>
<td>Darlan(^1)</td>
<td>1</td>
<td>Orange</td>
<td>---------------</td>
<td>5</td>
</tr>
<tr>
<td>Orlon(^2)</td>
<td>1</td>
<td>Yellow</td>
<td>More than 20</td>
<td>5</td>
</tr>
</tbody>
</table>

1. Staple Fibers  
2. Filament Yarn  
3. AATCC Test Method 16A-56, Test No. 3, (10)  
4. AATCC Test Method 61-54, (11)
CHAPTER III

DISCUSSION

This work was begun by reacting diazotized 2,4-dinitroaniline (diazotized by Method I) with acetic acid solutions of phenyldianilidophosphonamidate, tricresyl phosphate, triphenyl phosphite, and α-chlorophenyldiphenyl phosphate. The immediate formation of a red color in the solution containing phenyldianilidophosphonamidate was interpreted as an indication that coupling had occurred. The fact that a significant color change was not observed in the other three solutions was interpreted to mean that coupling had not occurred in these reaction mixtures.

In an attempt to increase the extent of coupling in the solution containing phenyldianilidophosphonamidate, and to effect coupling in the other three solutions, the pH of all four solutions was raised by the addition of sodium acetate. The effect of the sodium acetate was to increase slightly the depth of color in each solution.

Reactions with Tricresyl Phosphate.--Three additional experiments with tricresyl phosphate (described in the preceding chapter) in which tricresyl phosphate was reacted, in two different mole ratios, with diazotized 2,4-dinitroaniline (diazotized by two different methods) failed to yield a colored product with dyeing properties of sufficient interest to warrant further investigation at this time.
Reaction with Triphenyl Phosphite.—The one experiment described in Chapter II in which diazotized 2,4-dinitroaniline was reacted with triphenyl phosphite in a mole ratio of 1:1 yielded a product which colored nylon, acetate, Dynel, Orlon, Dacron, and Acrilan fibers.

A small portion of this sample, when boiled in a dilute solution of sulphuric acid in an attempt to effect a possible rearrangement of the product initially obtained, yielded an oily orange residue which dyed nylon a pale green color but had no effect on Orlon.

Because the product obtained from phenyldianilido-phosphonamidate was of considerably greater interest as a dyestuff than the oily product obtained from triphenyl phosphite, work with the latter compound was not pursued further.

Reactions with \(o\)-Chlorophenyldiphenyl Phosphate.—Reactions with \(o\)-chlorophenyldiphenyl phosphate with 2,4-dinitroaniline diazotized by two different methods, in a mole ratio of 1:1, yielded products which did not dye textile fibers (Experiments 1 and 2, Chapter II). The reaction of two moles of diazotized 2,4-dinitroaniline with one mole of the phosphorus intermediate (Experiment 3) yielded a brown crystalline product which dyed nylon, Orlon, and Dacron brown. However, this product had a deleterious effect on the textile fibers, which may have been due to the presence of unreacted starting material.
Work with this compound was not pursued further for the reason given above under triphenyl phosphite.

Reactions of Phenyldianilidophosphonamidate.

Diazotization of 2,4-Dinitroaniline.—In Chapter II five different methods for the diazotization of 2,4-dinitroaniline are described. Method 1 was taken from Saunders (6). The extremely low yield of product obtained when 2,4-dinitroaniline diazotized by this method was reacted with phenyldianilidophosphonamidate (Experiment 11, Chapter II) was believed due to instability of the diazonium salt. For this reason, Method 2 (7) for the diazotization of 2,4-dinitroaniline was adopted. In this method solution of the sodium nitrite is effected at a higher temperature than that used in Method 1, and the diazotized base was diluted with a controlled (maximum) amount of water.

The yield of colored product obtained with 2,4-dinitroaniline diazotized by Method 2 (Experiment 7, Chapter II) was not increased over that obtained in Experiment 11.

Diazotization by Method 4 (8) was adopted because the use of diazonium salt solutions prepared in pyridine permitted coupling in media at a higher pH.

In diazotization Methods 3 and 5, dilution with ice was omitted, to prevent precipitation of the extremely water insoluble phenyldianilidophosphonamidate.
Attempted Coupling of Phenylidianilidophosphonamidate with Diazotized 2,4-Dinitroaniline.—From each of the twelve experiments described in Chapter II, in which 2,4-dinitroaniline diazotized by five different methods was reacted with phenylidianilidophosphonamidate in mole ratios of 1:1 and 2:1, in acetic acid or pyridine solvents, a colored reaction product which dyed textile fibers was obtained. In all cases, the yield was extremely low, and we were unable to isolate the colored compound in pure form.

Experiment 1, in which diazotized 2,4-dinitroaniline was coupled in a mole ratio of 1:1 with phenylidianilidophosphonamidate in acetic acid solution containing sodium acetate, yielded a dark red crystalline solid. This product had the ability to dye nylon, Dacron, and acetate fibers from water solution at the boil; it was unnecessary to add any other reagents to the dye bath to effect this dyeing.

In order to increase the yield of colored compound obtained in Experiment 1, this experiment was repeated (Experiment 2) using 2,4-dinitroaniline diazotized by Method 2. The quantities of acetic acid and sodium acetate used were increased. A product consisting essentially of sodium acetate contaminated with a small amount of the desired product was obtained.

In the third experiment, Experiment 2 was repeated, except this time the sodium acetate was omitted. A small quantity of a reddish-orange crystalline material, essentially
completely soluble in hot water, was obtained. This water solution dyed nylon, Orlon, Dacron, Acrilan, Dynel, and acetate at the boil. Again, however, the yield of colored product was very small.

In an attempt to obtain a greater amount of the colored compound Experiment 4 was run. In this experiment the mole ratio of 2,4-dinitroaniline to phosphorus-containing intermediate was increased from 1:1, used in Experiment 3, to 2:1. This experiment yielded sufficient product to permit dyeing of a variety of textile fibers, and the dyed fibers were subjected to wash- and lightfastness tests. The results of these tests are summarized in Table I.

These tests were sufficiently encouraging to warrant synthesis of the product in amounts sufficient to permit analyses which could be used to elucidate its structure.

In one further small-scale experiment (Experiment 5) designed to increase the yield of the desired colored compound, a coupling was attempted in acetic acid using 2,4-dinitroaniline diazotized by Method 3. However, the desired result was not achieved.

A review of the work done to this point indicated that the best results were obtained with 2,4-dinitroaniline diazotized by Method 2, coupled in a mole ratio of 2:1 with phenyldianilidophosphonamidate in acetic acid solution. Therefore, Experiment 6 was run using one-tenth of a mole of the phosphorus-containing intermediate. This experiment
yielded the desired product which, after repeated re-
crystallization from hot water, melted sharply at 179°C.

Phosphorus determinations on this product indicated
the presence of about 1 per cent phosphorus. The results of
microchemical analyses for carbon, hydrogen, and nitrogen
indicated that the empirical formula for the substance was
C₆H₅N₃O₄ (the per cent oxygen was obtained by difference from
100; the phosphorus content was ignored.). The melting point
of 2,4-dinitroaniline is 180°C (12). A mixed melting point
taken on a mixture of this compound with 2,4-dinitroaniline
also melted at 179°C.

On the basis of the phosphorus determination, the mixed
melting point, the color of this compound and its infrared
absorption spectrum, it was assumed that the product was
essentially 2,4-dinitroaniline contaminated with a small
amount of a phosphorus-containing substance. The methods of
purification used in an attempt to isolate a phosphorus-
containing compound from this experiment yielded not the
desired product, but instead, impure 2,4-dinitroaniline.

The presence of 2,4-dinitroaniline in the product of
the reaction between diazotized 2,4-dinitroaniline and
phenyldianilidophosphonamidate may be attributed either to
its formation from a product formed as a result of reaction
between the starting materials (possibly during the re-
crystallization from hot water) or from incomplete diazotization
of the base initially.
The ability of the colored compound obtained from Experiment 6 satisfactorily to dye synthetic fibers may be due either to the chemical nature of the product itself or to the fact that it was mixed or combined with 2,4-dinitroaniline. The latter compound alone will impart a yellow tint to synthetic fibers from boiling aqueous solution. In combination with the phosphorus-containing compound, the aniline may be acting as a carrier or dyeing assistant, thereby making it possible for the fibers to accept the other product of this reaction as a dyestuff.

Experiments 7, 8, 9, and 10 were run simultaneously in an attempt to increase the yield of the desired product by using 2,4-dinitroaniline diazotized in pyridine. This made it possible to effect couplings in media of considerably higher pH than could be obtained when diazotizations were carried out in concentrated sulphuric acid alone.

All four of these experiments were run with a mole ratio of diazonium salt to coupling component of 1:1. In two of the experiments (7 and 8) the diazonium salt was diluted with water before coupling was effected; water was not used in Experiments 9 and 10. Experiments 7 and 9 were run in glacial acetic as solvents; Experiments 8 and 10 employed pyridine.

Of these four experiments, 7 and 9 looked best, and these were rerun on a larger scale, number 7 as Experiment 11
and number 9 as Experiment 12. In Experiments 11 and 12, both of which employed acetic acid as a solvent, the mole ratio of diazonium salt to phenylidianilidophosphonamidate was increased from 1:1, used in the preceding experiments, to 2:1.

Experiment 11 failed to yield significant quantities of a hot water soluble product which would dye textile fibers. Several products, all of which were capable of dyeing synthetic fibers, were isolated from Experiment 12. Unfortunately, none of these products was obtained in amounts sufficient to permit determinations of chemical identity.

On the basis of method of isolation, Sample 7 in Experiment 12 (base diazotized in pyridine) corresponds to the sample obtained in Experiment 6 (base diazotized in concentrated sulphuric acid without pyridine). The sample from Experiment 6 (recrystallized only from hot water) was assumed to be essentially 2,4-dinitroaniline contaminated with a small amount of the desired product. Extraction of Sample 7, Experiment 12, with benzene yielded, on the basis of color, 2,4-dinitroaniline purer than that obtained in Experiment 6.

It is interesting to note that in two instances in Experiment 12 in which solid products were extracted with benzene (Samples 2, M.P. 182-184°C.; and 7, M.P. 175-176°C.), the benzene soluble portion, obtained on evaporation of the solvent, yielded products of lower melting points (Sample 5,
M.P. 166-168°C., from Sample 2; and Sample 9, M.P. 155-156°C., from Sample 7).

Samples 5 and 6 which had similar melting points (166-168°C. and 163-165°C. respectively) and were similar in appearance were shown not to be identical on the basis of a mixed melting point (138-140°C.).

Attempted Coupling of Phenylidianilidophosphonamidate with Fast Salts.—In three exploratory experiments, attempts were made to couple phenylidianilidophosphonamidate with Fast Salts (diazotized and stabilized aromatic amines). Only the Fast Scarlet GG Salt (2,5-dichloroaniline) yielded a product of interest. The brown crystals obtained, which were insoluble in hot water, dyed nylon red from a solution of 95% ethyl alcohol.

Work with these intermediates was not pursued further.

Reaction of Phenylidianilidophosphonamidate with p-Nitroaniline.—The one experiment performed with diazotized p-nitroaniline gave results which were not of sufficient interest to warrant further work at this time.

Attempts to Condense 2,4-Dinitro-4'-Aminoazobenzene with Dichlorophenylphosphine Oxide.

Coupling of two moles of diazotized 2,4-dinitroaniline with 1 mole of phenylidianilidophosphonamidate in positions para to the two-NH-groups would yield:

\[ \left( \text{NO}_2 \right)_2 \text{C}_6 \text{H}_3 - \text{N} = \text{N-C}_6 \text{H}_4 \text{NH}_2 \text{P(O)} \text{C}_6 \text{H}_5 \]
This compound is also preparable, theoretically, by condensation of 2 moles of 2,4-dinitro-4'-aminoazobenzene with 1 mole of dichlorophenylphosphine oxide.

Two experiments were run in an attempt to effect this condensation. In one of these, (Experiment 2) pyridine was used as a condensing agent; in Experiment 1, an excess of the azo compound was used. From both experiments only unchanged starting material was isolated.
CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Colored products with dyeing properties of interest for use on synthetic fibers were obtained from attempted couplings of diazotized 2,4-dinitroaniline with phenyl-dianilidophosphonamidate. Of the twelve experiments described in Chapter II, Experiments 5 (diazotization in sulfuric acid, no water added; no water used to aid in isolation of the product), and 12 (diazotization in pyridine, no water added) yielded the most promising results.

It is recommended that Experiment 5 be repeated on a larger scale in order to obtain sufficient product for chemical identification. Diazotization using Method 2, but without the addition of water to the diazonium salt, and isolation of the product without first diluting with water should also be investigated.

Of all the experiments tried, Experiment 12, in which 2,4-dinitroaniline diazotized in pyridine was reacted with phenyl-dianilidophosphonamidate in glacial acetic acid, looks most promising. This work should be repeated to determine the nature of the products obtained.

The colored product obtained in Experiment 6 (Chapter II) by coupling diazotized 2,4-dinitroaniline with phenyl-dianilidophosphonamidate was found to be essentially
2,4-dinitroaniline which contained a small amount of the desired colored product. This result indicated that the method of purification to obtain the actual colored compound was not suitable. Consequently, it is recommended that other methods of purification, e.g., chromatographic adsorption, be attempted to isolate the desired compound.

The colored impurity was assumed to be a phosphorus-containing compound, on the basis of the results of a phosphorus determination. However, it is recommended that the phosphorus determination be rechecked, and that 2,4-dinitroaniline be analyzed simultaneously. The aniline itself may have given a false indication of the presence of phosphorus.

Phosphorus determinations are useful for determining whether or not coupling has been effected. Coupling of the reactants in a mole ratio of 1:1 should yield a product containing about 8% phosphorus; the product of a 2:1 coupling of diazonium salt with phosphorus-containing intermediate should contain about 4.5% phosphorus.

The dyeing properties of compounds obtained by reacting two moles of diazotized 2,4-dinitroaniline with one mole of o-chlorophenyldiphenyl phosphate should be investigated further. Purification of the product to remove unreacted starting material may yield a dyestuff which will not adversely affect textile fibers.
Triphenyl phosphite and diazotized 2,4-dinitroaniline yielded a colored product which may be of interest as a dyestuff. Consequently, it is recommended that this phosphorus-containing intermediate be investigated further.
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