191–192°, was obtained. The crystalline appearance and the melting point are substantially those of 2-methyl-9-phenyl-2,3,4,9-tetrahydro-1-pyridindene thiocyanate.[2]

Nitrate of 2-methyl-9-phenyl-2,3,4,4a-tetrahydro-1-pyridindene (XI). To the other 10-cc. portion mentioned above was added a supercooled solution of 3 g. of potassium nitrate in 5 cc. of water. After 30 min., the supernatant liquor was decanted from the oily precipitate which was digested for a few minutes with about 5 cc. of hot acetone. After standing for about 3 hr. at room temperature, the mixture was filtered. In this manner, 0.30 g. of solid, m.p. 173–175°, was obtained. After crystallization from ethanol, 0.185 g. of crystals melting at 176–179°, were obtained. The compound was further identified by its absorption spectrum as the nitrate of 2-methyl-9-phenyl-2,3,4,4a-tetrahydro-1-pyridindene (XI).[2]

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[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Nitrogen Compounds of the Phosphoric and Phosphonic Acids. III. Preparation and Properties of Amides of Phenylphosphonic and Phenylphosphonothioic Acids[1]

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Phenylphosphonic diamide, $C_6H_5PO(NH_2)_2$ (I), and the thioic diamide, $C_6H_5PS(NH_2)_2$ (II), can be prepared readily by interaction of the respective chlorides with liquid ammonia. Partial alcoholysis of (I) leads to formation of the alkyl P-phenylphosphonamidates, $C_6H_5PO(NH_2)(OR)$, where R = C_2H_5, n-C_3H_7, n-C_4H_9, and n-C_5H_{11}. Partial hydrazinolysis of (I) gives the phenylphosphonamidic hydrazide, $C_6H_5PO(NH_2)(N_2H_3)$, which reacts with p-methoxybenzaldehyde and with acetone to form the respective N^2-arylidene(alkylidene)phenylphosphonamidic hydrazides.

Only a limited number of unsubstituted amides of P-alkyl or -arylphosphonic acids have been described in the literature[4,5] and only one of the corresponding thioic compounds has been reported.[6] A convenient method for preparing phenylphosphonic diamide (I), and the previously unknown phenylphosphonothioic diamide (II) is given in the present paper. A new type of reaction by which alkyl P-phenylphosphonamidates, $C_6H_5PO(NH_2)OR$, are obtained by the alcoholysis of (I) is also described. The preparation of phenylphosphonamidic hydrazide by the hydrazinolysis of (I) is also discussed.

Both phenylphosphonic diamide (I) and phenylphosphonothioic diamide (II) were prepared in excellent yields by interaction of the corresponding dichlorides with liquid ammonia. It was found that (II) is much less stable toward hydrolysis than the oxo-analog.

The partial alcoholysis of (I) with ethyl, n-propyl, n-butyl, and n-amyl alcohols resulted in the formation of a new class of compounds that may be designated as alkyl P-phenylphosphonamidates, $RPO(NH_2)(OR)$ (III to VI, respectively). The compounds are solids that can be purified readily by recrystallization. There was no marked tendency for further alcoholysis to the ester to take place. The time required for reaction decreased with increasing molecular weight of the alcohol employed, presumably due in large measure to the progressively higher reaction temperature attained.

Hydrazinolysis of (I) gave phenylphosphonamidic hydrazide (VII), $C_6H_5PO(NH_2)N_2H_3$, in moderate yield. No phenylphosphonic dihydrazide was obtained in the reaction. The identity of (VII) was confirmed (*a*) by cryoscopic studies in water, (*b*) by the determination of the percentage of nitrogen present as hydrazine nitrogen, and (*c*) by conversion into aldehyde and ketone derivatives.

EXPERIMENTAL[7,8]

Phenylphosphonic diamide (I), $C_6H_5PO(NH_2)_2$. Attempts to prepare (I) by the method of Michaelis,[9] based upon the reaction of the acid chloride with concentrated aqueous

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[1] For the second article of this series see Smith, Gher, and Audrieth, *J. Org. Chem.*, **21**, 113 (1956).

[2] Abstracted from doctoral dissertation submitted to the Graduate College of the University of Illinois by W. C. Smith (1954).

[3] Victor Chemical Works Research Fellow at the University of Illinois, 1953–4; present address, Chemical Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Del.

[4] Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1950.

[5] Rätz, *J. Am. Chem. Soc.*, **77**, 4170 (1955).

[6] Michaelis, *Ann.*, **315**, 43 (1901).

[7] The analytical values for the percentage of carbon were outside experimental error in several instances, even though the other analytical values were quite satisfactory. Despite repeated efforts by Mr. J. Nemith, to whom the authors are grateful for carrying out microanalyses of compounds described in this and previous articles of this series, no method for attaining more acceptable values could be developed.

[8] Melting points are uncorrected.

[9] Michaelis, *Ann.*, **293**, 193 (1896).

ammonia, yielded only small amounts of the desired product. The desired compound was obtained in excellent yield, however, when liquid ammonia was employed. Phenylphosphonic dichloride[10] (97.5 g., 0.500 mole) was added dropwise with vigorous stirring, over a 1-hr. period, to 1 l. of liquid ammonia contained in a Dewar flask. A loose-fitting, plastic cover containing holes for the funnel tip and the stirrer shaft was placed over the flask to prevent spattering. The crude product was separated from the liquid ammonia mother liquor by filtration and the solid washed with two 100-ml. portions of liquid ammonia. The ammonia-insoluble solid was found to consist of essentially pure (I), melting sharply at 188°, and comprised the larger part of the yield of the desired reaction product. A few additional grams of (I) were obtained by evaporating the ammonia mother liquor to dryness, extracting the ammonium chloride with water, and recrystallizing the water-insoluble material from absolute ethanol. Recrystallization from water gave (I) that was suitable for use as a starting material for subsequent work (m.p. 188°C.); pure (I) melting at 191°C. could be obtained by recrystallization from absolute ethanol. The yield was 73.3 g. (94.1%).

Anal. Calcd. for $C_6H_9N_2OP$: C, 46.16; H, 5.81; N, 17.95. Found: C, 45.84; H, 5.76; N, 17.97.

Quantitative solubilities of (I) in g./100 g. of solvent at 25° were determined: water, 1.11; absolute ethanol, 0.392; diethyl ether, 0.006; chloroform, 0.011; carbon tetrachloride, 0.0025.

The attempted titration of (I) with 1*N* hydrochloric acid demonstrated that the compound was not sufficiently basic to form a salt when treated with a strong acid. An aqueous solution of (I) had a *p*H of 7.10. Treatment of an ethanolic solution of (I) with hydrogen chloride gas resulted in the cleavage of the P—N bond and the precipitation of ammonium chloride. Addition of (I) to 1*N* sodium hydroxide brought about the slow hydrolysis of the amide.

Phenylphosphonothioic diamide (II), $C_6H_5PS(NH_2)_2$. This compound, like its oxo-analog, could not be prepared by the reaction of the acid chloride with concentrated aqueous ammonia but could be made satisfactorily when liquid ammonia was employed. Phenylphosphonothioic dichloride[10] (106 g., 0.500 mole) was added slowly to one liter of liquid ammonia. The resulting ammonia solution was evaporated to dryness under a stream of dry nitrogen and the crude product extracted with one liter of warm diethyl ether. A portion of crude (II) was recovered by filtration after cooling the ether extract to 0°; the ether mother liquor was then used for two further extractions and subsequently concentrated to recover an additional small quantity of solid. Final recrystallization from ether gave plates melting at 41°. The yield was 72.2 g. (83.7%).

Compound (II) is very soluble in absolute ethanol. It dissolves in water readily with the concomitant formation of an oil that could not be crystallized. It was observed that (II) is quite unstable and that it is particularly sensitive to moisture. It decomposes very rapidly on standing in the atmosphere unless all of the diethyl ether is completely eliminated in the vacuum desiccator. However, even analytically pure samples of (II) were converted to gelatinous masses after standing in closed containers for several months. Results obtained on analysis of recrystallized (II) are given below.

Anal. Calcd. for $C_6H_9N_2PS$: C, 41.85; H, 5.27; N, 16.27. Found: C, 41.74; H, 5.55; N, 16.02.

Ethyl P-phenylphosphonamidate (III), $C_6H_5PO(NH_2)OC_2H_5$. A solution of (I) (10.0 g., 0.0642 mole) in absolute ethanol (400 ml., 6.87 moles) was held at reflux for 24 hr. The amount of ethanol employed was just sufficient to dissolve all of the (I) at the reaction temperature. One hundred ml. of xylene was then added to the alcoholic solution, the unreacted ethanol removed by distillation, and the crude product isolated by cooling the residual xylene solution. After washing the crude (III) with 25 ml. of diethyl ether the product was recrystallized from xylene as a colorless solid melting at 127°. The yield was 9.23 g. (90.1%). The product is soluble in hot absolute ethanol, hot water, chloroform, acetone, and hot xylene; it is moderately soluble in cold ethanol, and only slightly soluble in diethyl ether, cold water, and petroleum ether.

Anal. Calcd. for $C_8H_{12}NO_2P$: C, 51.88; H, 6.53; N, 7.56. Found: C, 52.53; H, 6.38; N, 7.59.

n-Propyl P-phenylphosphonamidate (IV), $C_6H_5PO(NH_2)OC_3H_7$. A slurry of (I) (10.0 g., 0.0642 mole) in redistilled 1-propanol (50 ml.; 0.668 mole) was heated at reflux for 24 hr. Complete solution occurred after 22 hr.; the temperature reached a maximum of 100° during the reflux period.[11] The bulk of the crude (IV) was isolated by concentrating the alcoholic solution to 40 ml. and cooling it to 0°. A small additional amount of (IV) was precipitated from the mother liquor by treatment with 75 ml. of diethyl ether. The amidate is soluble in absolute ethanol, water, carbon tetrachloride, and xylene, moderately soluble in diethyl ether, and slightly soluble in petroleum ether. Recrystallization of (IV) from carbon tetrachloride gave a colorless solid melting at 135°. The yield was 10.2 g. (74.3%).

Anal. Calcd. for $C_9H_{14}NO_2P$: C, 54.26; H, 7.08; N, 7.03. Found: C, 54.38; H, 6.97; N, 6.94.

n-Butyl P-phenylphosphonamidate (V), $C_6H_5PO(NH_2)OC_4H_9$. A slurry of (I) (10.0 g., 0.0642 mole) in redistilled 1-butanol (50 ml., 0.547 mole) was held at reflux for 8 hr. During the course of the reaction a maximum temperature of 110° was reached and (I) dissolved slowly. A trace of solid removed from the hot alcoholic solution by filtration was identified by its melting point as unreacted diamide. Crystallization could not be effected by cooling the filtrate; it was therefore concentrated to 40 ml., cooled, and treated with 40 ml. of petroleum ether (b.p. 100–110°). A substantial amount of product precipitated; further concentration of the alcoholic filtrate and treatment with petroleum ether (b.p. 100–110°) yielded several additional crops of crude product. The compound is soluble in absolute ethanol, 1-butyl alcohol, hot water, hot petroleum ether and hot carbon tetrachloride; it is moderately soluble in diethyl ether, slightly soluble in cold carbon tetrachloride or cold petroleum ether, and insoluble in cold water. The pure compound, recrystallized from carbon tetrachloride, melts at 104°. The yield was 11.0 g. (80.5%).

Anal. Calcd. for $C_{10}H_{16}NO_2P$: C, 56.32; H, 7.56; N, 6.57. Found: C, 56.37; H, 7.62; N, 6.32.

n-Amyl P-phenylphosphonamidate (VI), $C_6H_5PO(NH_2)OC_5H_{11}$. A slurry of (I) (10.0 g., 0.0642 mole) was heated at reflux with *n*-amyl alcohol (50 ml., 0.464 mole) for 7 hr. The diamide dissolved slowly during the reflux period and solution was complete after 6 hr. A maximum temperature of 130° was attained during the reaction; the development of a light brown color indicated that slight decomposition had taken place. As no solid precipitated on cooling to room temperature, the solution was concentrated to 40 ml., treated with 50 ml. of petroleum ether (b.p. 100–110°) and cooled to 0°. The crude (VI) that precipitated was separated by filtration and washed with two 25-ml. portions of diethyl ether. In order to recover additional product from the *n*-amyl alcohol solution, in which the former is appreciably soluble, it was necessary to remove the alcohol; this was accomplished by concentrating the mother liquor to 20 ml., adding 40 ml. of xylene and then again concentrating the solution to a volume of 35 ml. In this way most of the alcohol was removed and an appreciable amount of solid was recovered on cooling. Additional crude (VI) was recovered from the xylene filtrate by adding 50 ml. of petroleum ether (b.p. 100–110°), cooling the solution and filtering off the

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(10) The acid chlorides used in this investigation were kindly furnished by the Victor Chemical Works, Chicago, Ill., and were redistilled before use.

(11) A yield of only 40% was obtained if the reflux time was reduced to 12 hr.

solid fractions that formed on standing. The compound is soluble in *n*-amyl alcohol, absolute ethanol, hot petroleum ether, hot xylene, diethyl ether and hot water; it is moderately soluble in cold xylene, slightly soluble in cold petroleum ether and insoluble in cold water. The pure product, recrystallized from petroleum ether (b.p. 100–110°), melts at 82°. The yield was 8.99 g. (61.8%).

Anal. Calcd. for $C_{11}H_{18}NO_2P$: C, 58.11; H, 7.98; N, 6.16. Found: C, 58.48; H, 8.13; N, 6.08.

Phenylphosphonamidic hydrazide (VII), $C_6H_5PO(NH_2)$-N_2H_3. 1-Propanol[12] (96.2 ml., 1.29 moles) containing (I) (20.0 g., 0.128 mole) and 95% hydrazine (18.9 g., 0.564 mole; 12% excess) was heated at reflux for 15 hr. The diamide dissolved slowly during the course of the reaction,[13] and the temperature reached a maximum of 99°. The hot solution was filtered, the filtrate cooled in an ice bath and the resultant solid separated.[14] The product, which consisted largely of phenylphosphonamidic hydrazide, C_6H_5P-$(O)(NH_2)(N_2H_3)$, had crystallized as well formed monoclinic plates. It was washed on the filter with 200 ml. of diethyl ether, slurried with an additional 400 ml. of ether, and then placed under vacuum for 36 hr. to remove volatile contaminants. The compound is soluble in water, dimethylformamide, and hot absolute ethanol; it is recrystallized most satisfactorily from the latter solvent. The product was found to be slightly soluble in cold absolute ethanol, and is insoluble in chloroform, benzene, carbon tetrachloride, dioxane, diethyl ether, tetrahydrofuran, ethyl acetate, and acetonitrile. A silver mirror is formed when an aqueous solution of (VII) is treated with ammoniacal silver nitrate solution; a positive test for the presence of a reducing agent is also obtained on treatment with an iodine solution.

Melting point determinations in a capillary tube indicated that (VII) melts over a wide range on slow heating but would melt rapidly when immersed in a heating bath at temperatures substantially below those at which final melting occurred when the heating process was slow. These observations were confirmed by studying the behavior of (VII) on the hot stage of a microscope. When the compound is heated slowly beginning at room temperature, it melts over a range from 162–194°; it will melt rapidly when placed on the hot stage at 153° and will melt slowly but completely when placed on the stage at 143°.

Anal. Calcd. for $C_6H_{10}N_3OP$: C, 42.10; H, 5.89; N, 24.55. Found: C, 40.99; H, 5.88; N, 24.59.

The analytical results and the observations that have been recorded above could be applied equally well to a hydrazihydrazidate, with the formula $[C_6H_5PO(N_2H_3)$-$NH—]_2$. This possibility was eliminated (*a*) by determining the molecular weight of (VII) in water, (*b*) by analyzing for "hydrazine" nitrogen, and (*c*) by conversion to representative ketone and aldehyde derivatives, respectively.

The molecular weight of (VII) in water was determined cryoscopically. The determination was made as rapidly as possible in order to lessen errors caused by hydrolysis of the product. The apparent molecular weight values were found to come within 10% of the calculated value for (VII).

Anal. Calcd. for $C_6H_{10}N_3OP$: Mol. wt. 171.2. Found: Mol. wt. 175, 157, 156.

Samples of (VII) were dissolved in hydrochloric acid and titrated with a standard iodate solution using the method described in the first article of this series.[15] Duplicate samples of (VII), weighing 0.1066 g. and 0.1028 g., were found to require 24.71 and 24.10 ml. of 0.025*M* KIO_3, corresponding to 16.27 and 16.44% hydrazine nitrogen. The formula $C_{16}H_{10}N_3OP$ requires 16.35%.

Aldehyde and ketone derivatives [N^2-alkylidene(arylidene)phenylphosphonamidic hydrazides] were prepared by adding the carbonyl compound to a warm ethanolic solution of (VII). The *p*-methoxybenzaldehyde derivative was prepared in 84% yield, m.p. 163° (from chloroform).

Anal. Calcd. for $C_{14}H_{16}N_3O_2P$: C, 58.12; H, 5.58; N, 14.52. Found: C, 58.07; H, 5.64; N, 14.26.

The corresponding acetone derivative[16] was obtained in 79% yield, m.p. 193° (from acetone).

Anal. Calcd. for $C_9H_{14}N_3OP$: C, 51.18; H, 6.68; N, 19.90. Found: C, 51.36; H, 6.64; N, 19.54.

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[12] The reaction with hydrazine could not be carried out in the absence of a solvent. The actual function of the alcohol in this reaction was not determined.

[13] It was found that nearly all of the diamide could be recovered unchanged if the mixture was allowed to reflux for only three hr. Even after 12 hr. a large portion of the starting material could be recovered unchanged.

[14] The alcoholic filtrate from which the phenylphosphonamidic hydrazide had been removed was found to contain *n*-propyl phenylphosphonamidate, $C_6H_5P(O)$-$(OC_3H_7)(NH_2)$ (IV); this was recovered by treating the filtrate with 30 ml. of *n*-amyl alcohol and by then heating the solution carefully until all of the excess hydrazine had been eliminated. Needles of the ester crystallized when the hot solution was cooled; additional product was obtained on allowing the solution to stand. The compound was purified by recrystallization from carbon tetrachloride; its identity was confirmed (*a*) by melting point and (*b*) by comparison of the infrared spectrum with that of an authentic sample of (IV) prepared by the reaction of phenylphosphonic diamide and 1-propanol in the absence of hydrazine, as described in this article.

[15] Audrieth, Gher, and Smith, *J. Org. Chem.*, **20**, 1288 (1955).

[16] The melting point of 193° was observed on slow heating. However, this compound, like (VII), will melt on rapid immersion at temperatures as much as 15° below this value.