Reactions of Secondary Phosphine Sulfides

GRACE PETERS

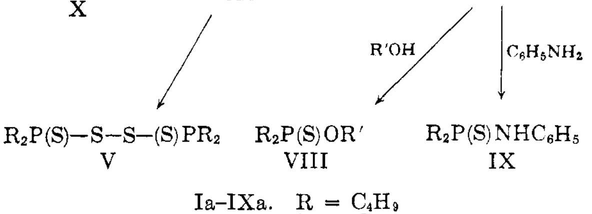
Chemical Research Department, Central Research Division, American Cyanamid Co., Stamford, Conn.

Received December 7, 1961

Secondary phosphine sulfides have been characterized by addition to carbonyl compounds, oxidation to dithiophosphinic acids, and conversion to thiophosphinyl chlorides.

In the preceding communication,[1] the successful preparation and preliminary characterization of a new class of compounds, the secondary phosphine sulfides (I), were reported. Further study has shown that some general reactions that these sulfides undergo are addition to carbonyl groups, oxidation, and chlorination, in which they reveal an analogy to the secondary phosphine oxides (II).[2] A synopsis of these reactions is presented in Chart I. Dibutylphoshine sulfide (Ia) was used as a model compound in many cases.

Oxidation.—Secondary phosphine sulfides can be oxidized by elemental sulfur to the corresponding dithiophosphinic acids (III) in good to excellent yields. The reaction was found applicable to aliphatic and aromatic phosphine sulfides and when coupled with their synthesis[1] forms an efficient route from a secondary phosphine to its dithioic acid derivative. Failure of early investigators[3-5] (who conducted the oxidation in one step) to obtain high yields stems from their isolation of the acids in the form of salts. Recently, improvements have been made in the preparation of ammonium dithiophosphinates by Rauhut and co-workers[6] through the use of aqueous ammonia as solvent. The present method complements the latter, gives the free acid directly, and is the method of choice for compounds sensitive to base or water. Only bis(2-cyanoethyl)dithiophosphinic acid proved too reactive to atmospheric moisture[7] to be isolated as a free acid. One other limitation was found: The use of excess sulfur is to be avoided, since further oxidation of the acids to the corresponding bis(dithiophosphinyl) disulfides (V) is possible.

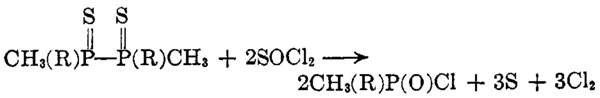


Ia–IXa. $R = C_4H_9$
VIIIa. $R' = i\text{-}C_3H_7$

Chart I

By contrast, the oxidation of dibutylphosphine sulfide (Ia) to dibutyl*thio*phosphinic acid (VIa) could not be accomplished. Attempted oxidation by iodine or hydrogen peroxide produced both dibutylphosphinic (IVa) and dibutyl*dithio*phosphinic (IIIa) acids, instead. Appearance and subsequent disappearance of colloidal sulfur during the reaction suggested that dibutylphosphine oxide (IIa) and sulfur were formed initially, only to undergo further reaction to produce the observed products. Depending upon reaction conditions, the disulfide Va was sometimes isolated instead of the dithiophosphinic acid. The possibility that small amounts of the desired thiophosphinic acid were actually formed but not detected cannot be excluded; however, hydrolysis of the thiophosphinyl chloride (*q.v.*) affords a more practical alternative.

Conversion to Thiophosphinyl Chlorides.—Although secondary phosphine oxides can be chlorinated directly to the corresponding phosphinyl chlorides, similar treatment of dibutylphosphine sulfide did not prove practical for preparing dibutylthiophosphinyl chloride (VIIa). Chlorine itself effected conversion in rather low yields, while chlorinating agents which are also potential oxidants caused replacement of the sulfur, as noted earlier by Maier[8] in his treatment of diphosphine disulfides with thionyl chloride.



$$CH_3(R)\overset{S}{\overset{\|}{P}}{-}\overset{S}{\overset{\|}{P}}(R)CH_3 + 2SOCl_2 \longrightarrow 2CH_3(R)P(O)Cl + 3S + 3Cl_2$$

An alternate method described by Schrader and

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[1] G. Peters, *J. Am. Chem. Soc.*, **82**, 4751 (1960).

[2] For a review on secondary phosphine oxides, see K. D. Berlin and G. B. Butler, *Chem. Rev.*, 243 (1960).

[3] A. W. Hofmann and F. Mahla, *Ber.*, **25**, 2436 (1892).

[4] L. Malatesta and R. Pizzotti, *Gazz. chim. ital.*, **76**, 167 (1946).

[5] L. Malatesta, *ibid.*, **77**, 509, 518 (1947).

[6] M. M. Rauhut, H. A. Currier, and V. P. Wystrach, *J. Org. Chem.*, **26**, 5133 (1961).

[7] M. M. Rauhut, H. A. Currier, G. A. Peters, F. C. Schaefer, and V. P. Wystrach, *J. Org. Chem.*, **26**, 5135 (1961).

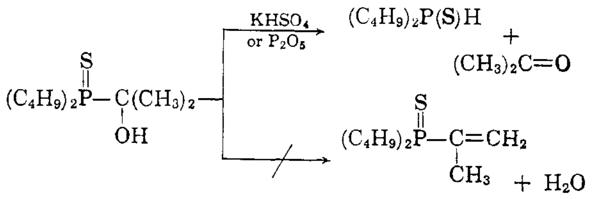
[8] L. Maier, *Angew. Chem.*, **71**, 575 (1959).

co-workers[9] using carbon tetrachloride and a tertiary amine was not satisfactory for isolating VIIa, because of competing side reactions. In the presence of isopropyl alcohol however, the chloride could be trapped as the thiophosphinate ester VIIIa.

The most practical method for preparing VIIa from dibutylphosphine sulfide was found to be conversion to the dithiophosphinic acid and subsequent chlorination by sulfuryl chloride (over-all yield 50–60%). A typical acid chloride, VIIa reacted with aniline to form the corresponding thiophosphinamide IXa, and with aqueous caustic to form the thiophosphinic acid VIa. Infrared examination of the latter indicated it exists in the thiono rather than the thiolo form, corroborating the study of phosphorus thio acids reported by Kabachnik and co-workers.[10]

Addition Reactions.—In direct analogy with the secondary phosphine oxides,[11] secondary phosphine sulfides undergo base-catalyzed nucleophilic addition to carbonyl compounds, forming α-hydroxy substituted tertiary phosphine sulfides (X). The solid products thus obtained can be purified by recrystallization, but the ready reversibility of the reaction rendered complete characterization of the liquid products impossible. However, the disappearance of the characteristic P—H infrared absorption band of I at 2320 ± 10 cm.$^{-1}$[11] and the concomitant appearance of primary, secondary, and tertiary alcohol bands[12] could be utilized to follow the course of the reaction. Thus, it was noted that the more reactive aldehydes such as chloral and formaldehyde required no catalyst, nor did phosphine sulfides with two electronegative substituents—*e.g.*, I. R = C_6H_5—, $NCCH_2CH_2$-, $C_2H_5OOCCH_2CH_2$—.

Two reactions of these tertiary sulfides (X) were studied briefly. The one was the attempted dehydration of acetone adducts, in which reversion to the original secondary phosphine sulfide took precedence over the desired reaction. The other was an extension of the Perkow rearrangement (as applied to phosphites) to the chloral adduct of dibutylphosphine sulfide (XI).



$$(RO)_2P(O)H + CCl_3CHO \longrightarrow (RO)_2P(O)CHOHCCl_3 \xrightarrow{\text{base}} (RO)_2P(O)OCH{=}CCl_2 + HCl$$

$$\begin{aligned}(C_4H_9)_2P(S)H + CCl_3CHO &\longrightarrow \underset{\text{XI}}{(C_4H_9)_2P(S)CHOHCCl_3}\\ &\longrightarrow (C_4H_9)_2P(S)OCH{=}CCl_2 + HCl\\ &\qquad\downarrow\\ &\quad + (C_4H_9)_2P(S)OC{\equiv}CCl + HCl\end{aligned}$$

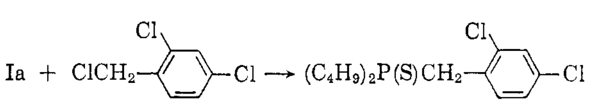
While dehydrohalogenation and rearrangement takes place, apparently not only one but also two moles of hydrogen chloride can be removed to produce both *O*-2,2-dichlorovinyl and *O*-chloroethynyl thiophosphinates in varying ratios depending upon the method of decomposition. With base, predominantly the vinyl derivative was obtained, and with heat, the ethynyl. Complete separation by distillation was not possible and identification was of necessity based on a composite of analytical determinations. For example, the major vapor phase chromatography component from the basic decomposition was found to contain two chlorine atoms (mass spectroscopy), butyl groups and a singlet H (NMR), and was assigned the vinyl structure. The thermal decomposition product was found to have butyl groups but no other hydrogens (NMR), and was distinguishable from the starting materials, and other possible rearranged products. Hence it was assigned to ethynyl structure. No further investigation of the scope of this reaction was carried out because of the separation difficulties encountered.

The addition of secondary phosphine sulfides to isocyanates and activated olefins such as acrylonitrile was investigated briefly. Although infrared examination indicated that addition had occurred, the products were difficult to purify and could not be satisfactorily characterized.

$$R_2P(S)H + R'NCO \xrightarrow{\text{base}} R_2P(S)CONHR'$$

$$R_2P(S)H + CH_2{=}CHCN \xrightarrow{\text{base}} R_2P(S)CH_2CH_2CN$$

Dibutylphosphine sulfide reacted with 2,4-dichlorobenzyl chloride to produce dibutyl-2,4-dichlorobenzylphosphine sulfide.



Experimental[13]

Dibutyldithiophosphinic Acid (IIIa).—A slurry of 17.8 g. (0.1 mole) of Ia[1] and 3.2 g. (0.1 g.-atom) of sulfur in 35 cc. of benzene was heated at reflux for 6 hr. The solution was filtered and stripped under reduced pressure to obtain 16.6 g. (79%) of crude product, containing no more P—H absorption in its infrared spectrum. Distillation of a portion gave a main cut, b.p. 144–146°/2 mm., $n^{28.5}_{\mathrm{D}}$ 1.5421 (lit., b.p. 99°/2 mm., n^{20}_{D} 1.5481).[10]

Anal. Calcd. for $C_8H_{19}PS_2$: P, 14.73; S, 30.49. Found: P, 14.65; S, 30.48.

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(9) G. Schrader, W. Lorenz, R. Cölln, and H. Schlör, Belgian Patent 576,811 (1958).

(10) M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov, and T. A. Melentyeva, *Tetrahedron*, **9**, 10 (1960).

(11) R. C. Miller, C. D. Miller, W. Rogers, Jr., and L. A. Hamilton, *J. Am. Chem. Soc.*, **79**, 424 (1957).

(12) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, 1954, p. 84.

(13) All melting points and boiling points are uncorrected. All reactions except hydrolysis and oxidation by iodine and peroxide were conducted under nitrogen.

Diisobutyldithiophosphinic Acid.—Diisobutylphosphine sulfide was oxidized *in situ* by stirring a mixture of 2.5 g. (0.017 mole) of diisobutylphosphine and 1.3 g. (0.04 g.-atom) of sulfur in 30 cc. of acetone overnight. After removal of excess sulfur and the solvent, 3.0 g. (84%) of product melting at 39° was isolated. Recrystallization from heptane gave needles, m.p. 39–40°.

Anal. Calcd. for $C_8H_{19}PS_2$: C, 45.68; H, 9.11; P, 14.73. Found: C, 45.85; H, 9.30; P, 14.47.

Diphenyldithiophosphinic Acid.—A mixture of 5.6 g. (0.03 mole) of diphenylphosphine and 1.9 g. (0.06 g.-atom) of sulfur in 50 cc. of benzene was heated at reflux for 6.5 hr. After filtration and stripping under reduced pressure, 6.8 g. (91%) of green oil was obtained, identical in infrared spectrum with a sample prepared by the method of Higgins.[14] In one run where an excess of sulfur was used, further oxidation occurred upon attempted crystallization of the oil from isopropyl alcohol, giving bis(diphenyldithiophosphinyl)-disulfide quantitatively. The disulfide melted at 146–147° after recrystallization from isopropyl alcohol-acetonitrile. No SH absorption at 2400 cm.$^{-1}$ characteristic of the acid remained in the infrared spectrum.

Anal. Calcd. for $C_{24}H_{20}P_2S_4$: P, 12.42; S, 25.72. Found: P, 12.70; S, 25.29.

Bis(2-cyanoethyl)dithiophosphinic Acid, Ammonium Salt.—Excess ammonia (50 cc.) was introduced at 10–20° into a mixture of 3.8 g. (0.12 g.-atom) of sulfur and 8.4 g. (0.06 mole) of bis(2-cyanoethyl)phosphine in 50 cc. of acetonitrile. The mixture was maintained at room temperature overnight. After the excess ammonia and solvent had been removed, 6.2 g. of product (47%), m.p. 147–150°, was obtained. Recrystallization from acetonitrile gave crystals, m.p. 163–165°.

Anal. Calcd. for $C_6H_{12}N_3PS_2$: C, 32.56; H, 5.47; S, 29.98. Found: C, 32.52; H, 5.41; S, 29.86.

In a similar reaction, the **cyclohexylamine salt** (4.3 g. = 47%) was isolated from the reaction of 1.9 g. (0.06 g.-atom) of sulfur and 4.2 g. (0.03 mole) of bis(2-cyanoethyl)phosphine in 5 cc. of cyclohexylamine, moderated in an ice bath. The melting point of the material crystallized from benzene was 123–124°.

Anal. Calcd. for $C_{12}H_{22}PS_2N_3$: N, 13.85; P, 10.20; S, 21.14. Found: N, 13.88; P, 10.07; S, 21.59.

Bis(dibutyldithiophosphinyl) Disulfide (Va).—Iodine (1.7 g. = 0.0075 mole) was added to 3.4 g. (0.015 mole) of ammonium dibutyldithiophosphinate[6] in 15 cc. of methanol, adapting the procedure of Malatesta and Pizzotti.[4] A total of 2.95 g. (94%) of product precipitated, m.p. 62–63° from methanol.

Anal. Calcd. for $C_{16}H_{36}P_2S_4$: C, 45.80; H, 8.67; P, 14.79; S, 30.74. Found: C, 46.13; H, 8.60; P, 15.17; S, 30.15.

This product was identical with one isolated in the treatment of 5.9 g. (0.032 mole) of Ia in 25 cc. of 1.4 *N* sodium hydroxide by 3.6 g. (0.016 mole) of iodine. Acidification of the aqueous layer after heating 6 hr. at 60° precipitated 0.9 g. of the disulfide. The organic layer did not solidify but decomposed upon attempted distillation.

Oxidation of Ia by Iodine.—Iodine (1.2 g. = 0.011 mole) was added with discharge of color to a solution of 2 g. (0.011 mole) of Ia in 5 cc. of ethanol containing a small amount of KI. The solution was filtered and stripped, leaving a brown liquid, from which the aniline salt of dibutyldithiophosphinic acid was obtained by treatment with a methanol solution of aniline. Yield of product, m.p. 110–111° from acetonitrile: 1.0 g. (67%) based on the equation:

$$2(C_4H_9)_2P(S)H + 2I_2 \xrightarrow{H_2O} C_4H_9)_2P(S)SH + (C_4H_9)_2POOH + 4HI$$

Anal. Calcd. for $C_{14}H_{26}PNS_2$: P, 10.21; N, 4.62. Found: P, 10.43; N, 4.59.

Oxidation of Ia by Hydrogen Peroxide.—A mixture of 4 cc. (0.01 mole) of 8.5% hydrogen peroxide and a few drops of acetic acid was added to 2 g. (0.011 mole) of Ia at 25°. An emulsion of sulfur formed. After 1.5 hr. at 90°, (starch iodide test negative) the reaction mixture was filtered and diluted with ice water. Extraction with ether gave 1.4 g. of oily residue upon concentration. Infrared examination suggested a mixture of the three possible acids, phosphinic, thiophosphinic, and dithiophosphinic, but only the aniline salt of dibutyldithiophosphinic acid, *v.a.*, was isolable upon treatment of the residue with aniline in methanol.

Dibutylthiophosphinyl Chloride (VIIa).—Method A. A benzene solution of crude dibutyldithiophosphinic acid prepared as above from 8.2 g. (0.046 mole) of Ia and 1.5 g. (0.046 g.-atom) of sulfur was concentrated to 15 g. To this was added drop-wise at 40–45° a solution of 4 cc. (0.048 mole) of sulfuryl chloride in 10 cc. of benzene. After 3 hr., 1.7 g. of sulfur (113%) was filtered and the filtrate was distilled to obtain a total of 5.2 g. (53%) of VIIa, b.p. 110–112°/1 mm., lit. 116°/1 mm.[9]

Anal. Calcd. for $C_8H_{18}PSCl$: Cl, 16.67; S, 15.07. Found: Cl, 16.39; S, 15.34.

Method B. Chlorine (23.4 g. = 0.165 mole) was distilled into a solution of 5.4 g. (0.03 mole) of Ia in 50 cc. of carbon tetrachloride at 15–20°. After 2 hours, distillation of the solution provided 1.1 g. (17%) of product, b.p. 130°/2 mm., identical with the material obtained by method A.

***N*-Phenyldibutylthiophosphinamide (IXa).**—A solution of 0.5 g. (0.0024 mole) of VIIa in methanol was treated with excess aniline. Removal of the solvent after the exothermic reaction subsided left a solid, which was filtered and washed with water and 10% hydrochloric acid. Two recrystallizations from hexane gave 0.2 g. (35%) of needles, m.p. 66–67°.

Anal. Calcd. for $C_{14}H_{24}PNS$: P, 11.50; S, 11.90; N, 5.20. Found: P, 11.57; S, 12.10; N, 5.21.

Dibutylthiophosphinic Acid (VIa).—The method of Schrader[9] was followed. From 2.3 g. of VIIa was obtained 1.8 g. of (85%) of yellow oil, from which an *aniline salt* was prepared by the addition of aniline in methanol. Recrystallized from heptane, the salt melted at 70–71°.

Anal. Calcd. for $C_{14}H_{26}NPOS$: C, 58.50; H, 9.12; N, 4.87; S, 11.16; P, 10.78. Found: C, 58.73; H, 9.02; N, 4.80; S, 11.28; P, 10.83.

***O*-Isopropyl Dibutylthiophosphinate (VIIIa).**—Three grams (0.03 mole) of triethylamine was added dropwise to a mixture of 5.3 g. (0.03 mole) of Ia and 4.6 g. (0.03 mole) of carbon tetrachloride in 10 cc. of isopropyl alcohol, while maintaining the exothermic reaction below 50°. The mixture was heated at reflux for 1 hr., cooled, and filtered to remove triethylamine hydrochloride. The residue upon removal of solvent from the filtrate under reduced pressure was extracted with benzene to remove any remaining salt. The crude product (2.4 g. = 34%) was distilled to obtain 0.5 g. (7%), b.p. 84°/0.1 mm. Decomposition was evident during the distillation.

Anal. Calcd. for $C_{11}H_{25}POS$: C, 55.90; H, 10.66; S, 13.57. Found: C, 55.79; H, 10.62; S, 13.69.

Dibutyl-2,4-dichlorobenzylphosphine Sulfide.—A solution of 1.0 g. (0.026 mole) of sodium hydroxide in 20 cc. of methanol was added dropwise to 4.7 g. of Ia and 5.2 g. of 2,4-dichlorobenzyl chloride (0.026 mole each) in 10 cc. of methanol. The mixture was maintained below 35° during the addition, but was heated at reflux for 2.5 hr. thereafter. After filtration of the sodium chloride, concentration of the filtrate left 3.7 g. (42%) of product, m.p. 60–62° from heptane.

Anal. Calcd. for $C_{15}H_{23}PSCl_2$: C, 53.41; H, 6.87; P, 9.18; S, 9.51. Found: C, 53.13; H, 6.96; P, 8.97; S, 9.61.

Diphenyl-1-hydroxy-1-methylethylphosphine Sulfide.—A mixture of 8.0 g. (0.04 mole) of diphenylphosphine and 3.6 g. (0.11 g.-atom) of sulfur in 40 cc. of acetone was allowed to react overnight at ambient temperature. Unchanged sulfur (1.6 g.) and excess solvent were removed to obtain 9 g. (75%) of product. Recrystallization from benzene gave purified

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[14] W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Am. Chem. Soc.*, **77**, 1864 (1955).

material, m.p. 118–120°, which could not be dried *in vacuo* without decomposition.

Anal. Calcd. for $C_{16}H_{17}POS$: C, 65.19; H, 6.20; S, 11.60. Found: C, 65.11; H, 6.99; S, 11.25.

Bis(2 - cyanoethyl) - 1 - hydroxy - 1 - methylethylphosphine Sulfide.—Following the procedure above, 14.0 g. (0.1 mole) of bis(2-cyanoethyl)phosphine and 3.2 g. (0.1 g.-atom) of sulfur interacted in 60 cc. of acetone to produce 16.1 g. (70%) of crude product. Recovery of material melting at 113–115° from benzene was 40%.

Anal. Calcd. for $C_9H_{15}N_2OPS$: C, 46.94; H, 6.57; N, 12.17; P, 13.45; S, 13.93. Found: C, 46.92; H, 6.51; N, 12.27; P, 13.39; S, 13.88.

Dibutyl-α-hydroxybenzylphosphine Sulfide.—A mixture of 2.0 g. (0.11 mole) of Ia, 1.2 g. (0.11 mole) of benzaldehyde, and 5 drops of triethylamine was allowed to react exothermically before adding 2 cc. of benzene and heating at reflux 3 hr. Removal of solvent left 2.5 g. (83%) of product, melting at 54–55° on recrystallization from heptane. A similar uncatalyzed reaction produced 2.9 g. (95%) of product in 2 days.

Anal. Calcd. for $C_{15}H_{25}POS$: C, 63.35; H, 8.86; S, 11.27. Found: C, 63.56; H, 8.98; S, 11.49.

Dibutyl-1-hydroxy-2,2,2-trichloroethylphosphine Sulfide (XI).—A third method of preparation is illustrated by the dropwise addition of 8.0 g. (0.055 mole) of dibutylphosphine at 25–30° to a slurry of 2.0 g. (0.06 g.-atom) of sulfur and 10.5 g. (0.07 mole) of chloral in 90 cc. of benzene. The mixture was heated briefly to 40° after the exotherm subsided. Unchanged sulfur (0.2 g.) was filtered, and the filtrate was stripped under reduced pressure to 21 g. (85% solution, maximum) of yeasty-smelling liquid to be used in the rearrangement below.

Rearrangement of XI. Method A. Base-Catalyzed.—The crude residue above, containing a maximum of 17.9 g. (0.055 mole) of XI, was dissolved in 20 cc. of methanol containing a trace of hydroquinone. A solution of 3 g. (0.055 mole) of sodium hydroxide in 16% aqueous methanol was added dropwise at 10°. After overnight stirring, 1.2 g. of sodium chloride was filtered and the neutral filtrate was stripped to $^1/_3$ volume, diluted with 75 cc. of ice water, and extracted with 125 cc. of methylene chloride. After drying over sodium sulfate, the extract was distilled to obtain a main fraction, 4.1 g., b.p. 145–152°/1 mm., containing by infrared and elemental analysis approximately 80% *O*-1,1-dichlorovinyldibutylthiophosphinate and 20% *O*-chloroethynyl dibutylthiophosphinate.

Anal. Calcd. for $C_{10}H_{19}PSOCl_2$: C, 41.53; H, 6.62; Cl, 24.52; P, 10.71. Found: C, 42.66; H, 7.61; Cl, 22.14; P, 11.03.

Separation by vapor phase chromatography gave a major fraction of mass 260 (theory 289) with two chlorine atoms. (Infrared analysis indicated some decomposition during the chromatographic separation.) NMR proton analysis of the original distillate showed the presence of a singlet H, in addition to the butyl grouping. Use of 2 moles of base per mole of XI produced material of approximately the same composition.

Method B. Thermal.—Distillation of 3.3 g. of XI gave a fraction, 0.3 g. b.p. 145–150°/0.25 mm., richer in the chloroethynyl ester. NMR analysis did not detect any H singlet, but elemental analysis suggested about 16% of the dichlorovinyl ester was present.

Anal. Calcd. for $C_{10}H_{18}PSOCl$: C, 47.52; H, 7.18; Cl, 14.03; S, 12.69. Found: C, 46.73; H, 8.18; Cl, 15.49; S, 12.22.

Acknowledgment.—For the analyses and interpretations thereof, the author is indebted to the following: infrared spectra, Mr. N. B. Colthup; mass spectra, Mr. A. H. Struck; NMR spectra, Dr. J. R. Lancaster; vapor phase chromatography, Dr. R. Feinland; and microanalyses, Dr. J. A. Kuck. For his constructive suggestions, we are also grateful to Dr. S. A. Buckler.

Reactions of Diethyl Phosphorochloridite with Alkali Salts of Nitroparaffins

TERUAKI MUKAIYAMA AND HIROHIKO NAMBU

Laboratory of Organic Chemistry, Tokyo Institute of Technology, Tokyo, Japan

Received December 19, 1961

Reactions of alkali salts of primary nitroparaffins with diethyl phosphorochloridite gave nitriles and diethyl hydrogen phosphate as the main products. On the other hand, when the sodium salt of 2-nitropropane was treated with diethyl phosphorochloridite, diethyl isopropylideneaminophosphate was obtained. Further, benzanilide was formed by the Beckmann rearrangement of the product from the reaction of the potassium salt of diphenylnitromethane and diethyl phosphorochloridite.

It was confirmed that the trivalent phosphorus of the initially formed condensation product, nitronic ester, was readily converted into the pentavalent phosphorus of the iminophosphate.

The preceding papers have described intramolecular dehydrations of primary nitroparaffins into nitrile oxides by means of isocyanates,[1] carbodiimides, and acetylenic ethers.[2]

In the present study, dehydrations of primary nitroparaffins with diethyl phosphorochloridite were tried first on the assumption that such compounds, reacting violently with water, were effective dehydrating reagents. It was expected that nitrile oxides and diethyl phosphorate would be formed *via* condensation compounds of *aci*-nitroparaffins and diethyl phosphorochloridite.

Contrary to our expectation, dehydrated products could not be obtained when diethyl phosphorochloridite was treated with the potassium salt of phenylnitromethane in boiling ether. Instead,

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(1) T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, **82**, 5339 (1960).

(2) T. Mukaiyama and T. Hata, *Bull. Chem. Soc. Japan*, **33**, 1382 (1960).