known, the following processes might reasonably be involved at one stage or another: oxidation and nuclear chlorination by ferric chloride, rearrangements of the phenylhydroxylamine or Bamberger[20] type.

Quite recently, Miller and White reported[21] the formation of hexachlorobenzene, together with a trace of chloranil, from the reaction of nitrobenzene with excess anhydrous ferric chloride at 190–195°.

Benzaldehyde. The reaction of benzaldehyde with ferric chloride or antimony pentachloride[22] resulted in the formation of dark, polymeric solid accompanied by the evolution of copious quantities of gas containing hydrogen chloride. In the case of ferric chloride, carbon monoxide[23,24] was also detected in the effluent vapor.

EXPERIMENTAL[25]

Antimony pentachloride and benzotrifluoride. Antimony pentachloride (144 g., 0.48 mole) was added slowly to benzotrifluoride (292 g., 2 moles) with stirring under nitrogen at 30–94° during 90 min. After 1 hr. at 90–95°, work-up of the reaction mixture, including refluxing with water, yielded benzoic acid (2 g.) and a liquid (21.2 g.), b.p. 57–58° (40 mm.), identified as chloro-α,α,α-trifluorotoluene (91% meta) by infrared analysis (authentic isomers as reference standards) and by hydrolysis[7] to m-chlorobenzoic acid, m.p., 152.5–153° from toluene; lit.[26] m.p. 153°.

Anal. Calcd. for $C_7H_5O_2Cl$: Neut. equiv., 156.6 Found: 157.

The liquid, 33.2 g., b.p. 105.5–106.5° (0.6 mm.), turned to a white solid, m.p. 49–50.5°. A mixture melting point with authentic m-benzoyl-α,α,α-trifluorotoluene from the ferric chloride-benzotrifluoride reaction showed no depression.

The distillation residue consisted of brown solid (9.1 g.).

Ferric chloride and benzotrifluoride.[27] A mixture of benzotrifluoride (2 moles) and anhydrous ferric chloride (1 mole) was heated under nitrogen at reflux for 4 hr. Work-up, including refluxing with water, yielded benzoic acid (6.6 g.) and m-benzoyl-α,α,α-trifluorotoluene, 29.6 g., b.p. 121–123° (1.5 mm.), m.p. 51.5–53° from aqueous methanol.

Anal. Calcd. for $C_{14}H_9F_3O$: C, 67.20; H, 3.62; F, 22.78. Found: C, 67.16; H, 3.77; F,[28] 23.14.

Hydrolysis of a portion of this fraction with sulfuric acid[7] gave a 95% yield (crude) of m-benzoylbenzoic acid, m p. 159.5–161° from toluene; lit.[29] m.p. 161°.

Anal. Calcd. for $C_{14}H_{10}O_3$: Neut. equiv., 226. Found: 228.

The distillation residue consisted of dark brown, brittle solid (60 g.).

Antimony pentachloride and nitrobenzene. A mixture of antimony pentachloride (69.9 g., 0.23 mole) and nitrobenzene (111.4 g., 0.91 mole) was heated at 108–118° under

nitrogen for 4.5 hr. Chloronitrobenzene, 23.5 g., b.p. 108.5–109.5° (11 mm.) was obtained. The product was a mixture of isomers, predominantly *meta*, as determined by infrared analysis.

Ferric chloride and nitrobenzene. A mixture of ferric chloride (0.5 mole) and nitrobenzene (1 mole) was heated during 4 hr. with stirring under nitrogen to 142° and then at 182–204° for 1 hr.

The reaction mixture was steam distilled and the steam-volatile material was fractionated, yielding a yellow liquid, 1.7 g., b.p. 103–105° (10 mm.), which was identified as a mixture of chloronitrobenzenes by comparison of the infrared spectrum with those of the authentic materials. The brown distillation residue (1.3 g.) was crystallized from toluene to yield 0.71 g. of chloranil, m.p. 289.5–290.5°; lit.[30] m.p. 290°.

Anal. Calcd. for $C_6Cl_4O_2$: C, 29.31; H, 0.00; Cl, 57.68. Found: C, 29.21; H, 0.06; Cl, 57.33.

The pot residue from steam distillation was made basic and the steam distillation continued. A small amount of solid (0.29 g.), m.p. 74.5–76° from dilute ethanol, was collected from the condenser. A mixture melting point with authentic 2,4,6-trichloroaniline showed no depression.

The remaining steam-volatile material was distilled to give a brown oil (0.1 g.), b.p. 64–96° (11 mm.). The infrared spectrum contained all the peaks of p-chloraniline, in addition to bands indicative of a nitro compound contaminant. Reaction of a portion of this fraction with benzoyl chloride gave a white solid, m.p. 188–190.5°, which did not depress the melting point of authentic N-(p-chlorophenyl)benzamide.

Antimony pentachloride and benzaldehyde. Antimony pentachloride (0.15 mole) was added to benzaldehyde (1.22 moles) at 120–156° under nitrogen. After 30 min. at 130–140°, work-up of the reaction mixture yielded black solid as the main product.

Anal. Found: C, 63.43; H, 3.96; Cl, 7.24.

The infrared spectrum of a gas sample collected over water during the early stages of reaction revealed no trace of carbon monoxide.

Ferric chloride and benzaldehyde.[31] A mixture of benzaldehyde (425 g., 4 moles) and ferric chloride (162 g., 1 mole) was heated under nitrogen at 145–160° for 1 hr. A gas sample[23] showed very weak infrared absorption bands of similar intensity at 2120 and 2180 cm.$^{-1}$, characteristic of carbon monoxide; lit.[32] 2135 and 2196 cm.$^{-1}$ (approx.). The reaction mixture yielded insoluble, infusible black solid (30 g.).

Anal. Found: C, 76.26; H, 3.22; Cl, 0.14 Fe, 0.73.

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(20) E. O. Bamberger, *Ann.*, **424**, 233, 297 (1921).

(21) R. E. Miller and W. A. White, *J. Org. Chem.*, **25**, 1249 (1960).

(22) R. Guehm and E. Bänziger, *Ann.*, **296**, 62 (1897).

(23) D. H. Hey, *J. Chem. Soc.*, **72**, (1935).

(24) H. E. Ungnade and E. W. Crandall, *J. Am. Chem. Soc.*, **71**, 2209 (1949).

(25) Melting points and boiling points are uncorrected; elemental analyses were performed by Drs. Weiler and Strauss, Oxford, England.

(26) J. C. Smith, *J. Chem. Soc.*, 213 (1934).

(27) F. J. Donat and C. K. Wilkins assisted with this experiment.

(28) We are indebted to the Dow Chemical Co. for this analysis.

(29) P. Senff, *Ann.*, **220**, 225 (1883).

(30) C. Graebe, *Ann.*, **263**, 16 (1891).

(31) Experiment performed by C. Wu.

(32) R. H. Pierson, A. N. Fletcher, and E. Gantz, *Anal. Chem.*, **28**, 1218 (1956).

Reaction of Organophosphorus Acids with Isocyanates[1]
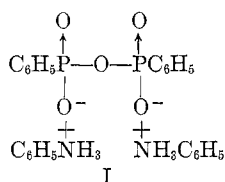
ROBERT B. FOX AND WILLIAM J. BAILEY

In a recent report,[2] it was shown that the tertiary amine salts of phenylphosphinie acid and the cor-

responding half-salts of phosphonic acids condense with isocyanates to give good yields the P- and O-carbamoyl derivatives, respectively. The acids themselves react with isocyanates and isocyanate adducts in quite a different manner, with the major isolated products being ureas and compounds formed by intermolecular dehydration of the phosphorus acids.

Such behavior is somewhat analogous to that observed by Naegeli and Tyabji[3] in the reactions of carboxylic acids with isocyanates, in which both ureas and anhydrides are formed along with amides and carbon dioxide. The carbon dioxide has been shown to arise from the isocyanate.[4]

We have found that both phenylphosphinic and phenylphosphonic acid react with phenyl isocyanate in an inert solvent at ordinary temperatures to give dianilinium diphenylpyrophosphonate (I) as the only isolable phosphorus containing product. The salt is readily hydrolyzed to a relatively un-

$$
\begin{array}{cc}
O & O \\
\uparrow & \uparrow \\
C_6H_5P\!\!-\!\!O\!\!-\!\!PC_6H_5 \\
| & | \\
O^- & O^- \\
+ & + \\
C_6H_5NH_3 & NH_3C_6H_5 \\
\end{array}
$$

I

stable acid which appears to be a dihydrate of diphenylpyrophosphonic acid. Upon being heated, this acid is rapidly converted to phenylphosphonic acid to produce water as the only volatile product of the reaction. The identity of I was confirmed through its independent preparation from aniline and the anhydrous diphenylpyrophosphonic acid formed by the restricted hydrolysis of phenylphosphonic dichloride.[5]

A facile method of synthesis of the salt I involves the reaction of phenylphosphonic acid and an isocyanate adduct, such as *sym*-diphenylurea or methyl carbanilate at about 210°. It is noteworthy that monoanilinium phenylphosphonate did not appear to dehydrate to give I at 210°, although the acid itself has been stated[6] to form diphenylpyrophosphonic acid at this temperature.

The mechanism of the formation of I from phenylphosphinic acid has not been elucidated with certainty, although it is apparent that an oxidation step is involved. Disproportionation of the acid to the phosphonic acid and phenylphosphine may be tentatively discounted on the basis of the lack of the very penetrating odor of the phosphine at any

point during the reaction. Yields of diphenylurea and of gases (probably carbon dioxide) absorbable by Ascarite were always high in the reactions with both the phosphinic and the phosphonic acid. It would be logical to assume that, analogously with the reactions of carboxylic acids,[3] I is formed through intermolecular dehydration of the phosphonic acid and subsequent reaction of the resulting acid with the aniline generated simultaneously from the isocyanate.

EXPERIMENTAL

Phenylphosphinic acid, m.p. 84°, and phenylphosphonic acid, m.p. 163.5–164°, were recrystallized commercial products. A Perkin-Elmer model 21 recording infrared spectrophotometer was used for the infrared spectra. Microanalyses are by Oakwold Laboratories, Alexandria, Va., Dr. Mary Aldridge, American University, and Mrs. Kathryn Gerdeman Baylouney, University of Maryland. All melting points are corrected, and those accompanied by decomposition gave a gas without sintering.

Reaction of phenylphosphinic acid with phenyl isocyanate. To a stirred suspension of 71.0 g. (0.5 mole) of phenylphosphinic acid in 750 ml. of dry toluene in an ice bath was added dropwise in a 45 min. period 71.4 g. (0.6 mole) of phenyl isocyanate. During the addition, much of the solid dissolved. In the course of stirring in the ice bath for an additional 2 hr. a precipitate formed; the evolution of a gas was evident throughout the reaction, and these gases were allowed to pass through an Ascarite tube. After being allowed to stand at room temperature overnight, the mixture was stirred 2 hr. at 75° and then 1 hr. at 100°. A total of 15.4 g. of a product was absorbed by the Ascarite tube. Filtration and concentration of the reaction mixture afforded 85.6 g. of crude crystalline material (an oily residue was discarded), which upon repeated recrystallization from hot isopropyl alcohol gave, in addition to diphenylurea, m.p. 248° dec., 25.0 g. (10%) of dianilinium diphenylpyrophosphonate, m.p. 211–213° dec.

Anal. Calcd. for $C_{24}H_{26}N_2O_5P_2$: C, 59.47; H, 5.31; P, 12.79. Found: C, 59.98; H, 5.18; P, 11.91.

The use of other inert solvents or a variation in reactant ratios had an adverse effect on the yield. In acetone, the reaction followed a different course and gave an unidentified *acid*, m.p. 199.5–200°, which may have been $C_6H_5P(O)$-$(OH)C(CH_3)_2OCONHC_6H_5$, but was not further characterized.

Reaction of phenylphosphonic acid with phenyl isocyanate. To a stirred solution of 15.8 g. (0.1 mole) of phenylphosphonic acid in 100 ml. of dry acetone at room temperature was added as rapidly as possible 13.1 g. (0.11 mole) of phenyl isocyanate. Within 30 min. the mixture had warmed slightly and an Ascarite tube appended to the reflux condenser had become quite hot, indicating the efflux of an absorbable gas. After the mixture had been heated under reflux for 2 hr., filtration and further concentration gave 22.0 g. of crude solids; the Ascarite tube gained 5.2 g. Repeated recrystallization of the crude material (which contained about 50% diphenylurea) from hot isopropyl alcohol gave a product, m.p. 210–212°, which on the basis of its infrared spectrum and a mixed melting point determination, appeared identical with the dianilinium diphenylpyrophosphonate obtained from phenylphosphinic acid.

Anal. Calcd. for $C_{24}H_{26}N_2O_5P_2$: C, 59.47; H, 5.31; P, 12.79; N, 5.78. Found: C, 60.70; H, 5.28; P, 12.00; N, 5.89.

Reaction of phenylphosphonic acid with phenyl isocyanate adducts. A mixture of 7.9 g. (0.05 mole) of phenylphosphonic acid and 10.6 g. (0.05 mole) of *sym*-diphenylurea was heated at 210° for 10 min. in an open test tube with a thermometer-stirring rod. One recrystallization of the cooled reaction

(1) Based on a portion of a thesis submitted in June 1959 by Robert B. Fox to the Graduate School of the University of Maryland in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

(2) R. B. Fox and W. J. Bailey, *J. Org. Chem.*, **25**, 1447 (1960).

(3) C. Naegeli and A. Tyabji, *Helv. Chim. Acta*, **17**, 931 (1934); **18**, 142 (1935).

(4) A. Fry, *J. Am. Chem. Soc.*, **75**, 2686 (1953).

(5) L. Anschütz and H. Wirth, *Chem. Ber.*, **89**, 688 (1956).

(6) A. Michaelis and C. Mathias, *Ber.*, **7**, 1070 (1874).

mass from 2.5 l. of hot isopropyl alcohol afforded 7.5 g. (62%) of dianilinium diphenylpyrophosphonate, m.p. 215–217°, identified through a comparison of its infrared spectrum with that of an authentic specimen.

A repetition of this experiment with methyl carbanilate in place of the urea gave similar results.

Dianilinium diphenylpyrophosphonate (1). A mixture of 5.5 g. (0.028 mole) of phenylphosphonic dichloride and 0.76 g. (0.042 mole) of water in 35 ml. of ether was shaken for 45 min., with occasional cooling under a water tap. Most of the volatile material in the resulting heavy oil was removed under water-aspirator pressure. Treatment with 10 ml. of cold water gave a crystalline precipitate which was washed with cold water, slurried with ether, and dried in air to yield without further purification, 2.3 g. (55%) of slightly hygroscopic diphenylpyrophosphonic acid, m.p. 81.5–82.5°^{5}.

Anal. Calcd. for $C_{12}H_{12}P_2O_5$: C, 48.30; H, 4.06; neut. equiv., 149.1. Found: C, 47.87; H, 4.04; neut. equiv., 150.4.

The dianilinium salt of this acid was prepared by the addition of 3 drops of aniline to a solution of 0.2 g. of the acid in 2 ml. of cold water; the resulting precipitate was recrystallized from hot isopropyl alcohol. The infrared spectrum and properties of this salt are identical in every respect with those of the salt prepared as described above. Aqueous solutions of dianilinium diphenylpyrophosphonate are acidic and fairly stable. Titration with alkali shows a sharp break at pH 8.5 with a neutralization equivalent of 241 ± 1 (calcd. 242).

An attempt to prepare this salt by heating a sample of monoanilinium phenylphosphonate (m.p. 210–213° dec.) at 210° failed to show evidence of dehydration. The infrared spectra of this salt and that of dianilinium diphenylpyrophosphonate are quite dissimilar.

Hydrolysis of dianilinium diphenylpyrophosphonate. A mixture of 2 g. of the dianilinium salt and 20 ml. of 10% aqueous sodium hydroxide was heated just to the boiling point, cooled, and extracted with ether to remove aniline (identified as acetanilide, m.p. 113–114°, and benzenesulfonanilide, m.p. 110–111°). Careful treatment of the aqueous alkaline solution with excess concentrated hydrochloric acid caused the precipitation of a crude acid, m.p. 75–77° dec. Recrystallization from *cold* acetone gave material, m.p. 82.5–83°, which was titrated as a strong monobasic acid with a neutralization equivalent of 169 ± 2 (calculated for diphenylpyrophosphonic acid dihydrate, 167). Crystallization of this substance from hot acetone gave material which exhibited a neutralization curve with two unequally spaced breaks. The infrared spectrum of the volatile material obtained by heating a sample of the acid at 100° showed the presence only of water. The spectrum of the residue or of a sample recrystallized from boiling toluene was identical with that of phenylphosphonic acid.

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The Reactions of Sodium Dialkyl Phosphonates with Carbonyl Sulfide and with Carbon Disulfide

DANIEL W. GRISLEY, JR.

The nucleophilic characteristics of the alkali metal dialkyl phosphonates, especially toward carbonyl groups,[1] prompted an investigation of their reactivity toward carbonyl sulfide and toward carbon disulfide. It was found that both reagents reacted with sodium dialkyl phosphonates to form a new phosphorus-carbon bond. The salts (I) and (II) were not isolated, but were allowed to react further to produce the corresponding thiolformate (III) and dithioformate (IV) esters. Structure III
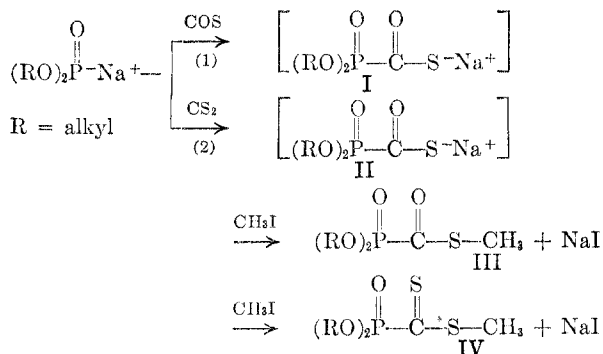
(R = ethyl) was indicated by a carbonyl absorption in the infrared spectrum at 6.15^2 μ. In addition, the NMR peak of III (R = ethyl) at +4.6 p.p.m., is within the range of the structurally similar acyl phosphonates which have a chemical shift of + 2 ± 1 p.p.m.[3] Finally, *S*-methyl diethoxyphosphinylthiolformate was amidated to yield the known amide (V) in 75% yield.[4] Diethoxyphosphinylformamide had characteristic amide carbonyl (6.0 μ) and N–H (3.0 μ and 3.15 μ) peaks in its infrared spectrum.[5] The NMR spectrum of V had a single peak at +1.4 p.p.m.
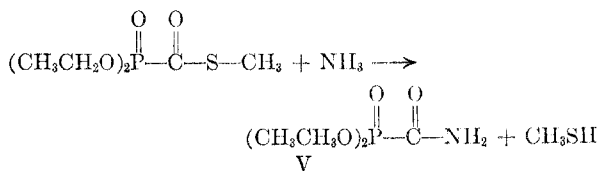
It was found that *S*-methyl diethoxyphosphinylthiolformate was easily dealkylated with sodium iodide to yield *O*-ethyl-*O*-sodium carbomethylthiophosphonate (VI). The NMR peak of VI
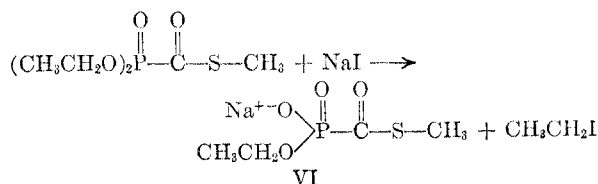
(1) A. N. Pudovik, *Uspekhi Khim.*, 23, 547 (1954).

(2) It is stated in L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, Inc., New York, 1954, p. 160, that the carbonyl frequencies of a number of thiol esters occur at 1675 cm.$^{-1}$ (5.96 μ).

(3) J. Van Wazer, C. Callis, J. Shoolery, and R. Jones, *J. Am. Chem. Soc.*, 78, 5715 (1956).

(4) P. Nylen, *Ber.*, 57, 1023 (1924).

(5) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Son, Inc., New York, 1954, p. 176 indicates the carbonyl absorption of primary amides at 1650 cm.$^{-1}$ (6.06 μ).