

separated, which had the appearance of crystallized copper sulfate. The substance melted at 280°, with formation of a dark olive green melt. For analysis, the crystals were dried over P₂O₅ in a vacuum.

Anal. Calcd. for CuSO₄·3C₃H₇N₂·H₂O (381.8): N, 22.0; S, 8.4. Found: N, 21.7; S, 8.5.

3. Ethylenediamine-Copper Sulfates. (a) 1:1 Chelate.—Anhydrous ethylenediamine (3.33 ml. = 0.05 mole) and 6.25 g. of CuSO₄·5H₂O (0.025 mole) were dissolved in a small amount of water. A few ml. of alcohol and dioxane were added, and the solution was kept in a refrigerator. Deeply violet-colored crystals appeared and were separated by decantation. Treatment of these crystals with a small amount of water, followed by filtration, gave a solution which yielded dark violet crystals on addition of dioxane and cooling in the refrigerator. The product was recrystallized from water-dioxane. The crystals obtained became light blue after drying. They did not melt when heated to 295°. Analysis showed that the product obtained was a mixture of approximately 9 parts of the 1:1 chelate and 1 part of the 1:2 chelate.

Anal. Calcd. for: CuSO₄·(H₂NCH₂CH₂NH₂)_{1.1}·1.5H₂O (252.6): N, 12.7; S, 12.2; Cu, 25.2; C, 10.5; H, 4.7. Found: N, 12.6; S, 12.3; Cu, 25.2; C, 11.2; H, 4.6.

(b) 1:2 Chelate.—From the mother liquor of the 1:1 chelate the 1:2 chelate could be isolated as dark violet colored crystals which also failed to melt when heated up to 295°.

Anal. Calcd. for CuSO₄·(H₂NCH₂CH₂NH₂)₂ (279.7): C, 17.2; H, 5.8; N, 20.5; Cu, 22.8; S, 11.5. Found: C, 17.2; H, 6.0; N, 19.4; Cu, 23.15; S, 11.5.

4. α,α'-Dipyridyl-Copper(II) 1:1 Chelates. I. Sulfates. (A) Acid Form (Diaqua Chelate).²³—Three and a half grams (0.014 mole) of CuSO₄·5H₂O in 25 ml. of water was added to 2.0 g. (0.013 mole) of dipyridyl and the flask was shaken vigorously. The resulting light blue precipitate was filtered off and washed with water. When recrystallized from boiling water needle-like prisms were obtained. When examined with the polarized light microscope they showed parallel extinction. The crystals did not melt but charred when heated to temperatures of between 250 and 300°. A solution of 22 mg. in 20 ml. of water had a pH of 5.4. For analysis the crystals were dried over P₂O₅ *in vacuo*.

Anal. Calcd. for C₁₀H₈N₂·CuSO₄·2H₂O (351.8): Cu, 18.1; S, 9.1; C, 34.3; H, 3.43; N, 8.1. Found: Cu, 18.1; S, 9.4; C, 34.1; H, 3.3; N, 7.8.

(B) Alkaline Form (Hydroxo Aqua Chelate).—To an aqueous suspension of 1 g. (0.0028 mole) of the complex pre-

(23) The isolation of this product had been described before by F. Blau, *Monatsh.*, **19**, 647 (1898).

pared above there was added 27.3 ml. of 0.0104 *N* NaOH. The solid dissolved and a dark blue solution resulted. The filtered solution was concentrated by vacuum evaporation. Recrystallization of the blue solid from boiling water gave large, well-formed, blue, rhombic crystals. They were dark between crossed prisms of the polarizing microscope when their diagonals were parallel to the crosshairs of the eyepiece (symmetrical extinction). A solution of 22 mg. in 20 ml. of water had a pH of 8.0. The crystals lost water when heated in a sealed capillary, decomposing at 225°, and were insoluble in organic solvents. For analysis they were dried over P₂O₅ *in vacuo*.

Anal. Calcd. for (C₁₀H₈N₂)₂(CuOH)₂SO₄·2H₂O (605.4): Cu, 21.0; S, 5.3; C, 39.6; H, 3.7; N, 9.3. Found: Cu, 21.2; S, 5.6; C, 39.9%; H, 3.8; N, 9.3.

Bubbling CO₂ into a warm saturated solution of the alkaline complex gave the blue needle-like prisms of the acid complex described in (A) above.

II. Acetates. (A) Acid Form.—A solution of 2.53 g. (0.0127 mole) of Cu(C₂H₃O₂)₂·H₂O in 25 ml. of water was added to 2.0 g. (0.0127 mole) of dipyridyl. A violet solution resulted which was evaporated to dryness *in vacuo* and the solid recrystallized from water plus a large volume of acetone. The dark violet needle-like prisms which were obtained showed parallel extinction when examined between crossed prisms of a polarizing microscope. When dried in air the crystals shrunk and changed to light blue in color. They decomposed at 196–201°, were very soluble in water or ethanol and only slightly in acetone. The 0.1% aqueous solutions had a pH of 6.1.

For analysis the substance was dried at 100° *in vacuo*.

Anal. Calcd. for C₁₀H₈N₂·Cu(C₂H₃O₂)₂ (337.7): Cu, 18.9; C, 49.7; H, 4.2; N, 8.3. Found: Cu, 19.2; C, 49.3; H, 4.5; N, 7.9.

B. Alkaline Form.—To 2.0 g. (0.0056 mole) of the above complex there was added 54 ml. of 0.104 *N* NaOH. Acetone was added to the dark blue aqueous solution. Upon cooling a crop of small, poorly-formed blue crystals was obtained. The 0.1% aqueous solution had a pH of 8.6. When dried over P₂O₅ *in vacuo* the crystals became bluish green.

Anal. Calcd. for C₁₀H₈N₂·Cu(C₂H₃O₂)·OH·H₂O (313.8): Cu, 20.3; C, 45.9; H, 4.5; N, 8.9. Found: Cu, 21.0; C, 46.2; H, 4.3; N, 8.6.

Acknowledgment.—The authors wish to thank Dr. G. M. Steinberg, Cml C Medical Laboratories, for valuable help in the organization and preparation of the manuscript.

(24) Combustion in the presence of V₂O₅.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, VICTOR CHEMICAL WORKS]

A New Method of Preparation for Alkenylphosphonous Dichlorides and Alkenylthionophosphonic Dichlorides

BY E. N. WALSH, T. M. BECK AND W. H. WOODSTOCK

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The reaction products of phosphorus pentachloride with certain olefins are reduced by elemental phosphorus only in the presence of iodine or iodine-liberating compounds to form the corresponding alkenylphosphonous dichlorides. The latter add sulfur to form the alkenylthionophosphonic dichlorides. Iodine also will catalyze the known reaction of olefin-phosphorus pentachloride addition compounds with phosphorus pentasulfide with a fivefold increase in yield of alkenylthionophosphonic dichlorides.

Introduction

Phosphorus pentachloride is known to add to certain olefins,^{1,2} to form the thermally unstable chloroalkylphosphorus tetrachlorides. Recently one of the authors³ described the reaction of such prod-

ucts with phosphorus pentasulfide to form alkenylthionophosphonic dichlorides, but the yields were always below 20%. Subsequent research has been undertaken to find an improved synthesis for alkenylthionophosphonic dichlorides and has resulted in two new preparative methods.

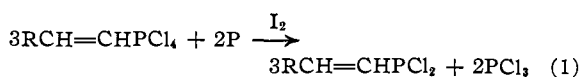
The first method entails a catalyzed reduction of the olefin-phosphorus pentachloride reaction products with elemental phosphorus to form the

(1) J. E. Marsh and J. A. Gardner, *J. Chem. Soc.*, **59**, 648 (1891).

(2) E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930); **64**, 1455 (1931); **66**, 278, 286 (1933).

(3) W. H. Woodstock, U. S. Patent 2,471,472.

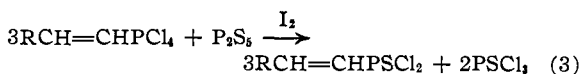
corresponding alkenylphosphonous dichloride, followed by the addition of elemental sulfur, according to equations 1 and 2.



Although equation 1 is analogous to a known reaction of phosphorus with phosphorus pentachloride, it proceeds only in the presence of catalytic amounts of iodine or iodine-liberating materials such as sodium iodide. Bromine and chlorine have no catalytic effect. To demonstrate through known compounds that the iodine-catalyzed reduction takes place in accord with equation 1, phenylphosphorus tetrachloride⁴ was allowed to react with phosphorus in the presence of iodine and was found to yield phenylphosphonous dichloride.

The addition of sulfur to the alkenylphosphonous dichlorides proceeds vigorously at elevated temperatures to give the desired compounds in good yields. The products are identical with the compounds obtained from the reaction of phosphorus pentasulfide with the analogous olefin/phosphorus pentachloride reaction products.

Iodine catalysis was applied subsequently to the reactions of olefin-phosphorus pentachloride reaction products with phosphorus pentasulfide, according to equation 3, and increased yields, up to five-



fold, were obtained. The role of the iodine catalyst in this reaction is not that of initiating a reaction which would not otherwise take place; rather, it causes reaction to proceed at lower temperatures with the elimination of side reactions which destroy much of the desired product.

A color change, of possible significance as to the mechanism of this catalysis, occurs in the phosphorus reduction reaction after the addition of iodine catalyst. A characteristic red color appears, which persists only as long as the olefin-phosphorus pentachloride reaction products and phosphorus are both present. A similar color reaction is observed in the iodine-catalyzed reaction of olefin-phosphorus pentachloride reaction products with phosphorus pentasulfide.

Experimental

I. Organophosphonous Dichlorides. A. Alkenylphosphonous Dichlorides. Isooctenylphosphonous Dichloride.⁵—Four hundred and twenty-eight grams (2 moles + 1.2 moles excess) of diisobutylene was added dropwise during a period of three hours at 0° to a well-agitated slurry of 417 g. (2 moles) of phosphorus pentachloride in 750 ml. of benzene. An exothermic reaction occurred with hydrogen chloride being liberated. The flask was flushed with carbon

dioxide and the stirring continued while a solution of 41.3 g. (1.33 moles) of white phosphorus in 8.0 ml. of carbon disulfide was added, followed by 0.2 g. of iodine crystals. The mixture was allowed to warm to 20° and the reaction then proceeded until all of the solids had reacted. Hydrogen chloride escaped from the exhaust tube throughout the experiment and cooling was needed to maintain the reaction temperature. The product was isolated by distillation; yield 281 g. (66%), n_D^{20} 1.5035, b.p. 70–72° (3 mm.). *Anal.* Calcd. for $\text{C}_8\text{H}_{15}\text{PCl}_2$: P, 14.5; Cl, 33.3. Found: P, 14.6; Cl, 33.1.

Similar results were obtained when solvents such as phosphorus trichloride and phosphorus oxychloride were employed. Solid white phosphorus can be used in place of the carbon disulfide solution. The presence of excess phosphorus presents a serious fire hazard, since any unreacted phosphorus distills with the solvent and the product. The same hazard also arises when the reaction mixture is allowed to warm to above 25° since chlorination of the olefin takes place, which results in a lowering of the yield and causes unreacted phosphorus to remain in the reaction mixture.

In the absence of iodine no product could be isolated from the reaction. However, iodine-liberating compounds such as sodium iodide and phosphorus triiodide were found to be as effective as iodine in catalyzing the reaction.

Styrylphosphonous Dichloride.—The reaction product of styrene and phosphorus pentachloride was prepared in 1000 ml. of phosphorus trichloride at 25° by adding 208 g. (1 mole + 1 mole excess) of styrene to 208.5 g. (1 mole) of phosphorus pentachloride. The reduction with phosphorus was carried out at 25 to 35° using the theoretical amount of white phosphorus. The yield of styrylphosphonous dichloride was 110 g. (53.6%), n_D^{20} 1.6350, b.p. 135–138° (8 mm.). *Anal.* Calcd. for $\text{C}_8\text{H}_7\text{PCl}_2$: P, 15.1; Cl, 34.7. Found: P, 15.1; Cl, 34.9.

A similar experiment was conducted using 1000 ml. of benzene as the solvent. This resulted in a product highly contaminated with what is presumed from the analytical data to be chlorostyrylphosphonous dichloride; yield 144 g., n_D^{20} 1.600, b.p. 135–138° (8 mm.). *Anal.* Found: P, 13.8; Cl, 39.1.

Isobutenylphosphonous Dichloride.—The reaction product of isobutene and phosphorus pentachloride was prepared by distilling 178 g. (2 moles + 1.2 moles excess) of isobutene into an agitated slurry of 417 g. (2 moles) of phosphorus pentachloride in 1000 ml. of benzene at 25°. The reduction reaction with phosphorus was conducted as described above. A yield of 212.2 g. of a mixture of isobutenylphosphonous dichloride and presumably, on the basis of the analytical data, chlorobutenylphosphonous dichloride was obtained. The mixture could not be separated by fractional distillation in a Vigreux column, nor could the chlorobutenylphosphonous dichloride be dehydrohalogenated without decomposition of the product; b.p. 98–104° (100 mm.), n_D^{20} 1.5087. *Anal.* Calcd. for $\text{C}_4\text{H}_7\text{PCl}_2$: P, 19.7; Cl, 45.2. Found: P, 18.5; Cl, 48.0.

Indenylphosphonous Dichloride.—This compound was prepared similarly to isooctenylphosphonous dichloride. The yield from 108.5 g. (0.5 mole) of phosphorus pentachloride was 30.0 g. (27.6%), b.p. 104–105° (1 mm.). *Anal.* Calcd. for $\text{C}_9\text{H}_7\text{PCl}_2$: P, 14.3; Cl, 32.7. Found: P, 13.1; Cl, 31.4. The product polymerized on standing.

B. Phenylphosphonous Dichloride.—One mole (179 g.) of phenylphosphonous dichloride was chlorinated in benzene to form a slurry containing phenylphosphorus tetrachloride. The reaction product was reduced with phosphorus in the presence of iodine to yield 171 g. (95.6%) of phenylphosphonous dichloride, b.p. 91–93° (6 mm.).

II. Preparation of Alkenylthionophosphonic Dichlorides. Procedure A. From Alkenylphosphonous Dichlorides.—A slurry of equimolar amounts of the alkenylphosphonous di-

PREPARATIONS OF STYRYL-, ISOÖCTENYL- AND ISOBUTENYLTHIONOPHOSPHONIC DICHLORIDES

Compound	Reacn. temp., °C.	Yield, %	°C.	B.p. Mm.	n_D^{20}	Phosphorus, %		Sulfur, %		Chlorine, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{C}_8\text{H}_7\text{PSCl}_2$	150	85	130	1	1.655	13.1	13.1	13.5	13.2	30.0	30.0
$\text{C}_8\text{H}_{15}\text{PSCl}_2$	175	87	95–100	2	1.5334	12.7	12.7	13.1	13.0	29.0	29.0
$\text{C}_4\text{H}_7\text{PSCl}_2$	200	79	115–125	30	1.5558	16.4	16.2	16.9	16.2	37.5	39.1

(4) A. Michaelis, *Ber.*, **6**, 816 (1873).

(5) The hydrocarbon radical is designated "isooctenyl" in the absence of a rigorous proof of structure.

chloride and sulfur was stirred and heated to the reaction temperature specified in the data given below. The mixture was maintained at this temperature until the heat of reac-

tion subsided and then for an additional ten minutes. The mixture was cooled and the product distilled.

Procedure B. From Olefin, Phosphorus Pentachloride and Phosphorus Pentasulfide.—The olefin-phosphorus pentachloride reaction products were prepared as described in section I. To the resulting slurry were added a catalytic amount of iodine and the theoretical amount of phosphorus pentasulfide. The reaction temperature was maintained at 25 to 50° until all of the solids had reacted and the solution was clear. The products were separated by distillation.

was complete. Styrylphosphinic acid was recrystallized from water.

The following table shows the results of these experiments.

Compound	M.p., °C.	Molecular wt. (titrn.)		Phosphorus, %	
		Calcd.	Found	Calcd.	Found
Styrylphosphinic acid	74-75	168	168	18.4	18.3
Isoöctenylphosphinic acid	Oil	176	176	17.5	17.5

PREPARATIONS OF STYRYL-, ISOÖCTENYL- AND ISOBUTENYLTHIONOPHOSPHONIC DICHLORIDES

Compound	Yield, %	B.p. °C.	Mm.	n_D^{20}	Phosphorus, %		Sulfur, %		Chlorine, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
C ₈ H ₇ PSCl ₂	51	130	1	1.6563	13.1	13.0	13.5	..	30.0	30.2
C ₈ H ₁₅ PSCl ₂	65	95-100	2	1.5330	12.7	12.5	13.1	13.0	29.0	29.7
C ₄ H ₇ PSCl ₂	95	115-125	30	1.5560	16.4	14.9	16.9	15.4	37.5	45.2

DI-*p*-NITROPHENYL DERIVATIVES OF ISOÖCTENYL- AND ISOBUTENYLTHIONOPHOSPHONIC DICHLORIDE

Compound	M.p., °C.	Phosphorus, %		Sulfur, %		Nitrogen, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C ₈ H ₁₅ PS(OC ₆ H ₄ NO ₂) ₂	81-82	6.9	7.0	7.1	7.1	6.2	6.2	0.0	0.0
C ₄ H ₇ PS(OC ₆ H ₄ NO ₂) ₂	103-105	7.9	7.9	8.1	8.1	7.1	7.2	0.0	0.0

The reaction was found to be highly exothermic; hydrogen chloride was evolved from the exhaust tube throughout the entire course of the reaction. Yields of over 80% styrylthionophosphonic dichloride have been obtained using procedure B but the resulting product contained from 2 to 3% excess chlorine. Purification by careful fractionation reduced this yield considerably.

Isobutenylthionophosphonic dichloride obtained by procedure A or procedure B is always contaminated with what is presumed from the analytical data to be chlorobutylthionophosphonic dichloride. The contaminant can neither be separated by fractional distillation in a Vigreux column nor can it be dehydrohalogenated without decomposition of the main product.

III. Hydrolysis of Alkenylphosphonous Dichlorides.—Ten grams of alkenylphosphonous dichloride was slurried in 100 ml. of concentrated hydrochloric acid until hydrolysis

Both acids are monobasic indicating the phosphinic acid structure.

IV. Derivatives of Alkenylthionophosphonic Dichlorides. Di-*p*-nitrophenyl Esters.—A mixture of 28.3 g. (0.2 mole) of *p*-nitrophenol, 21.6 g. (0.204 mole) of sodium carbonate and 0.1 mole of alkenylthionophosphonic dichloride was refluxed for four hours in 150 ml. of acetone. The product was isolated by pouring the mixture into water and extracting the compound with benzene. The product was recrystallized from benzene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. XVII. The Hydrolysis of 2,4-Dinitrobenzenesulfonyl Chloride

BY NORMAN KHARASCH, WILLIAM KING AND THOMAS C. BRUCE

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The hydrolysis of 2,4-dinitrobenzenesulfonyl chloride yields a variety of products, including 2,4-dinitrobenzenesulfenic anhydride, ArS-O-SAr (Ar = 2,4-dinitrophenyl), bis-(2,4-dinitrophenyl) disulfide (ArSSAr), 2-amino-4-nitrobenzenesulfonic acid, *m*-dinitrobenzene and 2,4-dinitrobenzenesulfonic acid. 2,4-Dinitrobenzene sulfenic acid is the probable precursor of all of these substances, but its isolation was not effected. A convenient synthesis of the 2-amino-4-nitrobenzenesulfonic acid, in 70% yield, also is described.

While 1-antraquinonesulfenic acid is the only example of this class of substances to have been isolated,¹ three selenenic acids, including 2,4-dinitrobenzeneselenenic acid,² have been reported. The hydrolysis of 2,4-dinitrobenzenesulfonyl chloride (I) was examined therefore as a possible route to 2,4-dinitrobenzenesulfenic acid (II, Ar = 2,4-dinitrophenyl).

Hydrolysis of I, in aqueous acetic acid at room temperature, occurred readily and with quantitative release of chloride ion; but instead of II, several products were found, including VII and IV (Ar = 2,4-dinitrophenyl, below) in major amounts,

and III, IV and VIII in smaller proportions. The formation of all of these substances can be interpreted conveniently on the basis that II is the unstable, first product in the hydrolysis of I.³ Compounds V and VI are also logical intermediates, but they were not isolated.

2,4-Dinitrobenzenesulfenic anhydride (IV) is a new product. It was characterized by elementary analysis, quantitative titration with iodide ion (ArS-O-SAr + 2H⁺ + 2I⁻ → ArS-SAr + I₂ + H₂O), conversion to acetyl 2,4-dinitrophenyl sulfide

(3) Cf. N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946); N. Kharasch and T. C. Bruce, *THIS JOURNAL*, **73**, 3240 (1951). For paper XVI of this series, cf. S. J. Assony and N. Kharasch, *Chem. and Ind.*, **45**, 1388 (1954).

(1) K. Fries, *Ber.*, **45**, 2965 (1912).

(2) O. Behaghel and W. Miller, *ibid.*, **68**, 1540 (1935).