[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, WESTVACO CHLOR-ALKALI DIVISION, FOOD MACHINERY AND CHEMICAL CORP.]

Preparation of Trichloromethylphosphonous Dichloride. Reduction of Tetrachlorophosphoranes with Methyl Phosphorodichloridite[1]

LOUIS D. QUIN[2] AND CHARLES H. ROLSTON[3]

Received May 16, 1958

Methylphosphonous dichloride was chlorinated in the cold to form tetrachloromethylphosphorane and then at higher temperatures to form tetrachloro(trichloromethyl)phosphorane. This compound was reduced by the action of methyl phosphorodichloridite to trichloromethylphosphonous dichloride.

A synthesis of trichloromethylphosphonous dichloride, heretofore unknown, has been accomplished. The method may be useful in obtaining other halomethyl phosphonous dichlorides.

In this synthesis, the unsubstituted phosphonous dichloride, CH_3PCl_2,[4] in an inert solvent is treated in the cold with chlorine. A quantitative yield of tetrachloromethylphosphorane, CH_3PCl_4, results. This compound, without isolation, is then chlorinated at 60–70° to produce tetrachloro(trichloromethyl)phosphorane. An earlier example of the smooth substitution of hydrogen in an alkyl tetrachlorophosphorane is the synthesis of this same trichloromethyl derivative by the chlorination of tetrachloro(chloromethyl)phosphorane[5]; the latter substance was formed from chlorine and chloromethylphosphonous dichloride, in turn obtained from diazomethane and phosphorus trichloride.[6]

The synthesis is completed by the reduction of the above tetrachlorophosphorane, again without isolation, to trichloromethylphosphonous dichloride in 85% over-all yield. We have introduced the use of methyl phosphorodichloridite, prepared from methanol and phosphorus trichloride,[7] for this type of reduction. Phosphorus[8,9] and certain metals[9] have previously been used for removal of chlorine from chlorophosphoranes and in fact we have used the former successfully in this reduction. The new reagent, however, is attractive because of the smoothness and simplicity of the reduction and ease of removal of its oxidation products, methyl chloride and phosphorus oxychloride, as well as any excess of the reagent. The reduction is postulated to proceed as follows:

$$CCl_3PCl_4 + CH_3OPCl_2 \longrightarrow CCl_3PCl_2 + CH_3OPCl_4 \tag{1}$$

$$CH_3OPCl_4 \longrightarrow CH_3Cl + POCl_3 \tag{2}$$

The exchange of chlorine in Equation 1 is facilitated by the decomposition of one of the products as shown in Equation 2. The literature[10] suggests such instability for CH_3OPCl_4, and this was established when an attempted preparation of this compound from chlorine and methyl phosphorodichloridite resulted in only the formation of methyl chloride and phosphorus oxychloride.

Tetrachloromethylphosphorane was also reduced smoothly by methyl phosphorodichloridite to the phosphonous dichloride in about 80% yield, and it is believed the reagent may be widely applicable for this type of reduction. The occurrence of a likely side-reaction (3) was not noted in the case where R

$$CH_3OPCl_2 + RPCl_4 \longrightarrow CH_3Cl + PCl_3 + RPOCl_2 \tag{3}$$

is $—CCl_3$ but may have occurred to a slight extent where R is $—CH_3$. Phosphites other than methyl phosphorodichloridite may also prove to be useful in the reduction of chlorophosphoranes.

The chlorination of methylphosphonous dichloride in concentrated solution or at temperatures above 30–40° is accompanied by some cleavage of the carbon-phosphorus bond. It is therefore an essential feature of the synthesis of trichloromethylphosphonous dichloride, and probably in any application of the synthetic method to the preparation of other substituted alkyl phosphonous dichlorides, that the starting material be stabilized in the form of the tetrachlorophosphorane. This derivative is chlorinated smoothly without bond cleavage, and the product is readily converted to the phosphonous dichloride. A variation of the classical principle of the protection of a sensitive functional group and its subsequent regeneration has thus been employed in this synthesis.

As is true of other phosphorus halides containing the strongly electronegative trichloromethyl group, trichloromethylphosphonous dichloride is resistant

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(1) Portions of this paper report work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C.

(2) Chemistry Department, Duke University, Durham, N. C.

(3) Explosives Department, E. I. du Pont de Nemours & Co., Gibbstown, N. J.

(4) F. W. Hoffmann and T. R. Moore, *J. Am. Chem. Soc.*, **80**, 1150 (1958).

(5) A. Y. Yakubovich and V. A. Ginsburg, *Zhur. Obshch. Khim.*, **24**, 1465 (1954).

(6) A. Y. Yakubovich, V. A. Ginsburg, and S. P. Makarov, *Doklady Akad. Nauk S.S.S.R.*, **71**, 303 (1950).

(7) D. R. Martin and P. J. Pizzolato, *J. Am. Chem. Soc.*, **72**, 4584 (1950).

(8) E. N. Walsh, T. M. Beck, and W. H. Woodstock, *J. Am. Chem. Soc.*, **77**, 929 (1955).

(9) W. A. Higgins, U. S. Patent **2,779,787**, Jan. 29, 1957.

(10) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 325.

to hydrolysis. In oxidation reactions, however, it reacts with vigor. It is oxidized rapidly on exposure to the atmosphere, and although much heat is generated, it does not inflame as has been reported for trifluoromethylphosphonous dichloride.[11]

EXPERIMENTAL

Preparation of tetrachloro(trichloromethyl)phosphorane. A solution of 234 g. (2.0 moles) methylphosphonous dichloride[4] in 600 g. phenylphosphonic dichloride as solvent[12] was stirred at 0° while 149 g. (2.1 moles) chlorine was added. The slurry of tetrachloromethylphosphorane was warmed to 60° and held there by cooling while 490 g. (6.9 moles) chlorine was added over a period of 3 hr. Chlorine consumption was complete until shortly before the stoichiometric amount (6.0 moles) had been added. The slurry was stirred at 55–60° under 100–150 mm. pressure to remove hydrogen chloride and excess chlorine. The product was not isolated but was used directly in the next step.

Preparation of trichloromethylphosphonous dichloride. The above reaction mixture was protected with nitrogen while 266 g. (2.0 moles) methyl phosphorodichloridite was added in 1.5 hr. The use of a small excess of this reagent causes no difficulty, but a large excess appears to reduce the yield. The mild exotherm was controlled to give a reaction temperature of 35°; higher temperatures cause slight yield reduction. Evolution of methyl chloride occurred near the end of the reaction as its solubility in the mixture was exceeded. The resulting clear solution was rectified *in vacuo* with a 0.75 in. by 15 in. column of Hastelloy B Heli-Pak. After a cut of phosphorus oxychloride, a 39-g. fraction, possibly a mixture of the chlorinated methylphosphonous dichlorides, was obtained over the range 63° at 30 mm. to 70° at 26 mm. Trichloromethylphosphonous dichloride was then collected at 69–70° at 23 mm. There was obtained 375 g. (1.70 moles), a yield of 85% on methylphosphonous dichloride charged. The still bottoms of phenylphosphonic dichloride were recovered for further use by simple distillation.

Trichloromethylphosphonous dichloride freezes at 47°[13] and boils at 171–172° [13] at 750 mm. It must be protected from the atmosphere, as oxidation occurs with great ease. It is insoluble in, and reacts only slowly with, water. It reacts quantitatively with chlorine to form tetrachloro(trichloromethyl)phosphorane.

Anal. Calcd. for CCl_5P: C, 5.45; Cl, 80.48; P, 14.07. Found: C, 5.23; Cl, 80.30; P, 14.33.

Reduction of tetrachloromethylphosphorane with methyl phosphorodichloridite. To a solution of 35.1 g. (0.30 mole) methylphosphonous dichloride in 300 g. chlorobenzene was added 22.0 g. (0.31 mole) chlorine. The temperature was held at 10° during this formation of tetrachloromethylphosphorane. The slurry was then warmed to 50° and treated over a period of 30 min. with 39.5 g. (0.30 mole) methyl phosphorodichloridite. The resulting clear solution was rectified. A 26.9-g. fraction of methylphosphonous dichloride (77% recovery) boiling at 81–82° was collected. In addition, a small forerun (5 g.) boiling from 77–81° was obtained; this probably contained more of the product along with phosphorus trichloride, formed as shown in Equation 3.

Attempted preparation of tetrachloromethoxyphosphorane. A solution of 40 g. (0.30 mole) methyl phosphorodichloridite in 265 ml. chlorobenzene was held below 10° while 22 g. (0.31 mole) chlorine was added. The exothermic reaction was completed in 45 min. Distillation was then conducted at reduced pressure (15–20 mm.) so as to maintain a pot temperature of 30°. Methyl chloride was evolved and collected in a Dry Ice trap. The distillate consisted of phosphorus oxychloride and the solvent. No residue remained after distillation. Tetrachloromethoxyphosphorane was thus shown to be unstable near room temperatures, decomposing cleanly according to Equation 2.

SOUTH CHARLESTON, W. VA.

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[11] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

[12] Available from Victor Chemical Works. This compound is inert in the reactions discussed and is used as solvent throughout; its high boiling point (258°) permits its use as a "chaser" in the distillation to isolate trichloromethylphosphonous dichloride. Other inert solvents are also useful.

[13] Uncorrected.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA AND THE RESEARCH DEPARTMENT, STAUFFER CHEMICAL CO.]

Derivatives of Sulfenic Acids. XXXIII. Studies of Thioperoxides. Part 4. Reactions of Trichloromethanesulfenyl Chloride with 1,2-Epoxides and Alcohols

ROBERT B. LANGFORD AND NORMAN KHARASCH

Received May 12, 1958

Trichloromethanesulfenyl chloride (I) reacts with 1,2-epoxides and with *meso*-1,2,3,4-diepoxybutane to form *beta*-chloroalkyl trichloromethanesulfenates. The reaction is catalyzed by tertiary amines, and identical products are obtained by substituting appropriate *beta*-chloro alcohols for the epoxides. The results agree with the mechanism which postulates *trans* opening of the epoxide rings, as previously suggested for the similar reactions of 2,4-dinitrobenzenesulfenyl chloride. The new products from reaction of I with epoxides and certain alcohols are reported.

Trichloromethanesulfenyl chloride (I) holds a unique position among aliphatic sulfenyl halides. Historically, it was the first of this group of substances to be reported,[1] its precise structure has been carefully investigated by infrared spectra,[2] and both the sulfenyl chloride and its derivatives have intrigued many industrial investigators.[3]

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[1] B. Rathke, *Ann.*, **167**, 204 (1873); *Cf.* also N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).

[2] J. A. A. Ketelaar and W. Vedder, *Rec. trav. chim.*, **74**, 1482 (1955).

[3] *Cf. e.g.* (a) A. R. Kittleson and H. L. Yowell, U. S. Patent **2,553,771** (1951); (b) G. H. Birum and R. J. Kern, U. S. Patent **2,769,777** (1956); and (c) E. M. Nygaard and J. H. McCracken, U. S. Patent **2,326,102** (1943).