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Preparation of Diphosphorus Tetrachloride¹

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Diphosphorus tetrachloride was prepared by conduction of an electrical discharge in gaseous mixtures of PCl_3 and H_2 or in PCl_3 vapor above solutions of PCl_3 and white phosphorus. In electrical discharges in PCl_3 - H_2 mixtures, the yield of P_2Cl_4 was found to be dependent on the mole ratio of PCl_3 to H_2 . A yield of 3.5 g./hr. was obtained using a mole ratio of 2 at a total pressure of 19 mm.; at a total pressure of 5 mm., a yield of 0.7 g./hr. was obtained using the same mole ratio. The mass spectrum of P_2Cl_4 for 70 e.v. electrons is reported. The n.m.r. spectrum using a frequency of 24.288 Mc./sec. gave a single peak with a chemical shift of -155 p.p.m. relative to 85% H_3PO_4 .

Introduction

Besson and Fournier² succeeded in preparing P_2Cl_4 by the reduction of PCl_3 with H_2 in a gaseous electrical discharge. Heretofore attempts to reproduce this synthesis in our Laboratory³ and in others⁴ have been unsuccessful. It appeared to us that Besson and Fournier failed to define some critical experimental condition in their preparation. Small amounts of P_2Cl_4 have been prepared by reduction of PCl_3 in electrical arcs using zinc⁵ and mercury⁶ electrodes.

In this paper we report the preparation of P_2Cl_4 by three different techniques: (I) conduction of an electrical discharge in $\text{PCl}_3(\text{g})$ above the surface of white phosphorus-phosphorus trichloride solutions; (II) conduction of an electrical discharge in H_2 above the surface of $\text{PCl}_3(\text{l})$; and (III) conduction of an electrical discharge in a homogeneous mixture of $\text{PCl}_3(\text{g})$ and H_2 . Critical experimental conditions have been found for the preparation of P_2Cl_4 from $\text{PCl}_3(\text{g})$ and H_2 in an electrical discharge. Chemical processes involved in the formation of P_2Cl_4 are postulated and a structure for P_2Cl_4 is proposed.

Experimental

Materials.—Reagent grade PCl_3 was purified by vacuum fractionation four times through a -45° bath into a trap at -78° . White phosphorus was washed with 6 *N* HNO_3 and H_2O , and placed in a tube containing solid CO_2 . The tube was joined to an adapter on the reaction vessel by a glass joint and sealed with Kel-F polymer wax (Minnesota Mining & Manufacturing Co.). The white phosphorus was dried under vacuum and distilled into the reaction vessel. The distillation tube then was sealed off from the system. Hydrogen gas was passed over hot copper shavings and dried by passing through a -196° bath.

Apparatus.—The reaction vessel consisted of a 100-ml. 3-necked round bottom flask with ground glass joints. Molybdenum electrodes were sealed to the inner part of the glass

joints with tungsten leads. The reaction vessel was connected to the vacuum system by an adapter with a stopcock. An 8-mm. tube was sealed to the adapter for the purpose of distilling phosphorus into the reaction vessel. A different adapter was used to introduce H_2 into the reaction vessel and to allow continuous removal of unreacted H_2 and volatile reaction products.

The high voltage source consisted of a 15,000-v. luminous tube transformer. The input voltage was varied to obtain voltages from 0 to 15,000 v.

Discharge Reaction Technique.—In the preparation of P_2Cl_4 from white phosphorus, 5 to 7 g. of phosphorus and 30 to 50 ml. of PCl_3 were introduced into the reaction vessel. The reaction vessel was closed, detached from the vacuum system, and immersed in a 0° bath. The electrodes, 2 to 5 cm. apart, were located 2 mm. above the surface of the liquid. A discharge voltage of 4000 to 7500 v. was used. To prevent heating of the reaction vessel, the high voltage was turned off for varying fractions of a ten-second cycle by a motor-driven variable time switch. The reactions were run for several hours with mild agitation of the reaction liquid.

In experiments employing an electrical discharge in $\text{PCl}_3(\text{g})$ and H_2 above the surface of liquid PCl_3 , the flow of H_2 into the reaction vessel was regulated by means of a needle valve. The reaction vessel was immersed in a constant temperature bath to obtain the desired pressure of PCl_3 . The unreacted H_2 and HCl were continuously removed from the reaction vessel during reaction.

The H_2 was bubbled through PCl_3 in experiments employing an electrical discharge in a homogeneous mixture of $\text{PCl}_3(\text{g})$ and H_2 . The flow of H_2 was adjusted by means of a needle valve. The pressure of PCl_3 in the saturated H_2 was regulated by temperature control of the PCl_3 bubbler. The PCl_3 - H_2 mixture was delivered into the reaction vessel, which was immersed in a -78° bath. A potential of about 7500 v. was used to maintain the electrical discharge. The unreacted H_2 and HCl were continuously pumped out. The procedure described by Finch⁶ was used to separate PCl_3 from P_2Cl_4 .

Spectral Data.—The mass spectrum of P_2Cl_4 was obtained with a Bendix time-of-flight mass spectrometer previously described.⁷ The n.m.r. spectrum of P_2Cl_4 was obtained with a Varian Associates HR-60 high resolution spectrometer equipped with a phosphorus probe and operated at a frequency of 24.288 Mc./sec. Eighty-five % H_3PO_4 contained in a capillary tube placed in the 5-mm. sample tube was used as a reference standard.

Results

Conduction of an electrical discharge for 3-hr. periods at a potential of 7500 v. above the surface of PCl_3 -P(white) solutions gave P_2Cl_4 yields of 1.5 g. In several experiments the PCl_3 -P(white) solutions were

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(2) A. Besson and L. Fournier, *Compt. rend.*, **150**, 102 (1910).

(3) D. W. Setser, H. C. Moser, and R. E. Hein, *J. Am. Chem. Soc.*, **81**, 4162 (1959).

(4) V. Gutmann, *Monatsh. Chem.*, **86**, 98 (1954).

(5) A. Stock, A. Brandt, and H. Fisher, *Chem. Ber.*, **58**, 643 (1925).

(6) A. Finch, *Can. J. Chem.*, **37**, 1793 (1959).

(7) E. J. Gallegos and R. W. Kiser, *J. Am. Chem. Soc.*, **83**, 773 (1961).

replaced by red phosphorus suspensions in PCl_3 . The yields of P_2Cl_4 in the latter experiments were very inconsistent, ranging from 0.1 to 4.0 g. for 7-hr. reaction periods.

The results of the two other techniques of preparation of P_2Cl_4 are given in Tables I and II.

TABLE I

CONDUCTION OF ELECTRICAL DISCHARGE IN H_2 ABOVE $\text{PCl}_3(1)$

$T, ^\circ\text{C.}$	$P, \text{mm.}$	Potential, v.	$t,$ hr.	Yield, g. P_2Cl_4
-78	1.3	5400	2.5	1.0
-21	6.0	4400	0.5	0.7

TABLE II

CONDUCTION OF ELECTRICAL DISCHARGE IN HOMOGENEOUS MIXTURE OF H_2 AND $\text{PCl}_3(\text{g})$

$P, \text{mm.}$	$P, \text{mm.}$	Potential, v.	$t,$ hr.	Yield, g. P_2Cl_4
13.0	6.0	7500	2.00	7.0
3.3	1.5	4200	3.25	2.2

In these experiments only the P_2Cl_4 was measured. The amount of red phosphorus formed was estimated to be about the same as the P_2Cl_4 . The same reaction vessel was used for successive reactions without removal of the red phosphorus. If the pressure of the H_2 in the discharge increased above the pressure of PCl_3 , larger quantities of red phosphorus deposited on the walls. Conduction of an electrical discharge in H_2 at atmospheric pressure saturated with PCl_3 at 25° yielded only red phosphorus and HCl .

The P_2Cl_4 had the properties already reported in the literature^{2,6}; however, we observed a melting point closer to -28° , the value reported by Besson, than to -34° , the value reported by Finch. The density was 1.701 g./cc. at 0° . The vapor pressure was approximately 1 mm. at 25° . *Anal.* Calcd. for P_2Cl_4 : P, 30.5; Cl, 69.5. Found: P, 29.7; Cl, 70.3. The appearance of m/e peaks corresponding to P_2Cl_4^+ ion in the mass spectra confirmed previous molecular weight determinations.⁶ The principal ions and their relative abundances in the mass spectrum for 70 e.v. electrons are given in Table III. There were minor peaks corresponding to PCl_3^+ and P_4^+ ; however, their absence from some spectra led us to believe their origin was from

TABLE III
MASS SPECTRUM OF P_2Cl_4

m/e	Relative abundance at 70 e.v.	m/e	Relative abundance at 70 e.v.
31	20.0	134	1.0
35	13.5	136	1.0
37	3.8	167	5.0
62	10.8	169	5.0
66	36.5	171	1.8
68	9.5	173	~0.0
97	6.0	202	4.6
99	3.0	204	7.3
101	100.0	206	4.0
103	65.0	208	1.5
105	11.2	210	~0.0
132	1.5		

the decomposition of P_2Cl_4 before introduction into the mass spectrometer. The chlorine-37 provided a convenient internal m/e reference. The n.m.r. spectrum of P_2Cl_4 showed a single peak. The chemical shift relative to 85% orthophosphoric acid was found to be -155 p.p.m.

Discussion

Conduction of an electrical discharge in a homogeneous mixture of $\text{PCl}_3(\text{g})$ and H_2 proved to be the best method for the preparation of P_2Cl_4 . Higher yields than those reported in this paper might be obtained when higher pressures of both PCl_3 and H_2 are used. The yield of P_2Cl_4 prepared by conducting the discharge above the surface of PCl_3 -P(white) solutions is limited because chlorine reacts with both P_4 and P_2Cl_4 contained in the liquid phase. Conducting the discharge in H_2 above the surface of liquid PCl_3 is not efficient because of ineffective mixing of H_2 with PCl_3 .

The formation of P_2Cl_4 from $\text{PCl}_3(\text{g})$ and H_2 in electrical discharges is critically dependent on the relative amounts of PCl_3 and H_2 regardless of the total pressure. Conduction of an electrical discharge in mixtures of PCl_3 and H_2 in which the mole ratio of PCl_3 to H_2 is very large leads predominantly to the formation of PCl_5 and red phosphorus. Under these conditions there is not sufficient reducing agent to prevent the oxidation of P_2Cl_4 or its precursors by chlorine. If the mole ratio of PCl_3 to H_2 is very small complete reduction to HCl and red P results. Between these two extremes we have obtained excellent yields of P_2Cl_4 using a mole ratio of 2/1 (PCl_3 to H_2) at total pressures of 5 or 19 mm. Interestingly, a mole ratio of 2/1 (PCl_3 to H_2) represents the stoichiometric amount of H_2 necessary to reduce PCl_3 to P_2Cl_4 . The complete reduction of PCl_3 by hydrogen in electrical discharges when the mole ratio of PCl_3 to H_2 is much smaller than 2 has led us to believe that molecular hydrogen reacts with the primary fragments produced in the discharge.

The n.m.r. spectrum of P_2Cl_4 established that the phosphorus atoms are identically bonded. The large relative abundance of PCl_2^+ ion in the mass spectra of P_2Cl_4 suggested the rupture of a weak bond in the homolytic dissociation of P_2Cl_4 . The bond energy for this dissociation has been determined to be 58 kcal./mole.⁸ The bond energy for the (P-P) single bonds in P_4 is 48 kcal./mole⁹; the (P-P) single bond without steric strain is estimated to be 3 to 6 kcal./mole higher.⁹ Apparently the phosphorus atoms in the P_2Cl_4 molecule are bonded to each other and to the chlorine atoms by $\sigma 3p$ single bonds.

On the basis of present information we propose a structure for P_2Cl_4 similar to that of P_2I_4 ¹⁰ in which the two sets of halogen atoms are positioned *trans* to each other.

(8) A. A. Sandoval, H. C. Moser, and R. W. Kiser, *J. Phys. Chem.*, **67**, 124 (1963).

(9) T. L. Cottrell, "The Strengths of Chemical Bonds," Second Ed., Butterworths Scientific Publications, London, 1958.

(10) Y. C. Leung and J. Waser, *J. Phys. Chem.*, **60**, 539 (1956).

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Synthesis of Mono-, Di-, and Triaminoborazines: Pyrolysis of Triaminoborazines

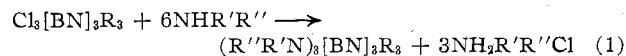
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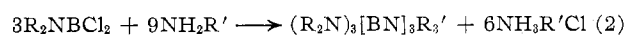
The B-triamino-, B-tris-(methylamino)-, and B-tris-(dimethylamino)- derivatives of N-trimethyl- and N-triphenylborazine have been prepared and characterized. The compounds were pyrolyzed at temperatures to 400° and the volatile products examined. Ring opening decomposition and "normal" deamination were observed. B-Tris-(methylamino)-N-triphenylborazine underwent an irreversible transformation, without change in composition, at its melting point. This phenomenon may be due to isomerism. B-Chloro-B-dimethyl- and B-dichloro-B-methyl-N-trimethylborazine have been prepared by alkylation of B-trichloro-N-trimethylborazine with methylmagnesium bromide in ether solution. Treatment of the chloro compounds with ammonia, methylamine, or dimethylamine gave the corresponding B-aminoborazines. The B-aminoborazines were converted back to the chloro compounds by reaction with phosphorus trichloride. The infrared spectra and X-ray diffraction patterns of the aminoborazines are recorded.

Introduction

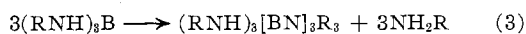
Methods for the synthesis of B-triaminoborazines have been reported in a patent by Gould¹ and in papers by Niedenzu and Dawson² and Aubrey and Lappert.³ Three distinct methods have been described: (1) reaction of a B-trichloroborazine⁴ with an excess of amine^{1,2}



(2) reaction of an aminodichloroborane with an excess of ammonia or primary amine²



and (3) pyrolysis of a triaminoborane³



Practical considerations exclude the applicability of the second and third methods for certain types of compounds. For example, neither method can be employed in the synthesis of the B-triaminoborazines $(H_2N)_3[BN]_3(R_3)$, while many primary amino derivatives, $(RHN)_3[BN]_3R'_3$, with different R and R' substituents, will be inaccessible through routes 2 and 3. The first method, however, is not subjected to these limitations. With a wide variety of B-trichloroborazines available,⁵ method 1 provides a convenient route to B-triaminoborazines.

The reactions of B-trichloroborazines with excess

ammonia, methylamine, and dimethylamine have been employed in the preparation of the B-triamino-, B-tris-(methylamino)-, and B-tris-(dimethylamino)- derivatives of N-trimethyl- and N-triphenylborazine. The synthesis of these compounds and the results of preliminary pyrolysis studies are reported here.

Grignard reagents have commonly been employed in the conversion of B-trichloroborazines to B-trialkyl- or B-triarylborazines.^{6,7} Ryschkewitsch, *et al.*,⁷ utilized a deficiency of Grignard reagent to butylate partially B-trichloro-N-trimethylborazine. They obtained B-dichloro-B-*n*-butyl-N-trimethylborazine, B-chloro-B-di-*n*-butyl-N-trimethylborazine, and B-tri-*n*-butyl-N-trimethylborazine. Their results indicated that, with respect to the Grignard reaction, the reactivity of each boron atom of the borazine ring was unaffected by substitution at the remaining boron positions. Hence, a more or less statistical distribution of products was obtained. Similar results were obtained with the corresponding B-ethyl-B-chloro derivatives, although no pure compounds were isolated.

It has now been found that the reaction of one mole of B-trichloro-N-trimethylborazine with one or two moles of methylmagnesium bromide in diethyl ether solution gives either B-chloro-B-dimethyl-N-trimethylborazine or B-dichloro-B-methyl-N-trimethylborazine, depending upon the amount of Grignard reagent employed. These results do suggest that methyl substitution on boron atoms alters the electronic environment about the other boron atoms in the borazine structure. Amination of the unsymmetrical chloroborazine with

(1) J. R. Gould, U. S. Patent 2,754,177 (July 10, 1956).

(2) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 356 (1959).

(3) D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.*, 2927 (1959).

(4) The notation $[BN]_3$ to designate the borazine ring was suggested by R. Didenko. Where no structural isomerism is possible, this notation is convenient and descriptive.

(5) L. F. Hohnstedt and D. T. Haworth, *J. Am. Chem. Soc.*, **82**, 89 (1960).

(6) (a) S. J. Groszos and S. F. Stafiej, *ibid.*, **80**, 1357 (1958); (b) D. T. Haworth and L. F. Hohnstedt, *ibid.*, **82**, 3800 (1960).

(7) G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *ibid.*, **80**, 4515 (1958).