ployed. In the first method, $BaCl_2$ in either natural or ^{18}O-enriched water was added within a few seconds of mixing the sodium tungstate and water, and barium tungstate was precipitated within 10–15 sec. The barium tungstate was filtered off and dried *in vacuo* at room temperature to give $BaWO_4 \cdot {}^1/_2H_2O$.

In the second method, sodium tungstate solutions were allowed to sit for 1 hr. or more and then were evaporated by vacuum distillation (until crystallization began) at 25° or at 30–50°. The $Na_2WO_4 \cdot 2H_2O$ was crystallized out either at room temperature or at 0°.

For the 12-tungstocobaltate(III), 1.72-g. samples of $K_4HCoW_{12}O_{40} \cdot 16H_2O$ were dissolved in 5.0 ml. of enriched water. The pH of the final solutions was 1–2 and the 12-tungstocobaltate was 0.1 *M*. Precipitation of the tetramethylammonium salt was carried out immediately by addition of excess tetramethylammonium bromide[3] in enriched water. The precipitate was dried *in vacuo* for 3 hr. at room temperature before being dried in a nitrogen stream at 200°.

Results and Discussion

The data on the experiments carried out by means of precipitation of $BaWO_4$ are summarized in Table II. All of the results for sodium tungstate in enriched water show complete exchange of oxygen between water and orthotungstate ion in the time required for mixing and separating the reagents. The one experiment in which the ^{18}O was introduced only in the $BaCl_2$ reagent suggests slightly less than complete exchange. It seems possible that the exchange might be studied by flow or other techniques for investigating moderately fast reactions.

Four experiments were carried out in which sodium tungstate was separated from the solution by distillation of solvent at reduced pressures, followed by crystallization of $Na_2WO_4 \cdot 2H_2O$. This was done to check for separation-induced exchange in the barium precipitation method. In one experiment the solution was evaporated in the 20–40° range and then was cooled in ice to hasten crystallization. The calculated equilibrium ^{18}O content was 1.41%; found, 1.50 ± 0.00%.

TABLE II

^{18}O CONTENT OF $BaWO_4$ PRECIPITATED AT 25° FROM Na_2WO_4 SOLUTION

$[Na_2WO_4] = 0.01\ M$, $[NaCl] = 1.0\ M$, $[BaCl_2]$ in precipitating reagent, 1.0 *M*

Soln.	Vol., ml.	pH	^{18}O content of H_2O in soln., atom %	^{18}O content of $BaWO_4$, atom % ± std. dev.
Na_2WO_4	25.25	11.0	1.57	
$BaCl_2$	3.50	7.0	0.20[a]	
Mixture	28.75		1.41[b]	1.38 ± 0.08
Na_2WO_4	25.25	11.0	1.57	
$BaCl_2$	3.50	7.0	0.20	
Mixture	28.75		1.41	1.42 ± 0.05
Na_2WO_4	25.25	11.0	1.58	
$BaCl_2$	3.50	12.0	0.20	
Mixture	28.75		1.41	1.55 ± 0.02
Na_2WO_4	25.25	11.0	0.204	
$BaCl_2$	3.50	12.0	1.46	
Mixture	28.75		0.354	0.266 ± 0.004
Na_2WO_4	12.5	12.0	1.46	
$BaCl_2$	1.75	12.0	0.20	
Mixture	14.25		1.31	1.42 ± 0.04
Na_2WO_4	25.00	12.0	1.46	
$BaCl_2$	3.50	12.0	1.46	
Mixture	28.40		1.46	1.48 ± 0.05
The sample below stood for 1.0 hr. before $BaWO_4$ precipitation				
Na_2WO_4	25.00	12.00	1.46	
$BaCl_2$	3.50	12.0	1.46	
Mixture	28.50		1.46	1.48 ± 0.006

[a] The content of our natural water and "Bone Dry grade" CO_2 was 0.206 ± 0.003%; the literature value is usually 0.204 (G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd Ed., John Wiley and Sons, New York, N. Y., 1964). [b] Calculated, assuming complete exchange.

In the other three experiments samples were maintained at room temperature for 1 hr. and also were held at 25.0° during evaporation. They were cooled in an ice bath during the crystallization. Two samples were run without added NaOH and at the pH of 11.0. In the first of these two experiments the calculated equilibrium ^{18}O content of the tungstate oxygen was 1.41%; found, 1.51 ± 0.02%. In the second the calculated was 1.40%; found, 1.43 ± 0.03%. In the final experiment, with 0.01 *M* NaOH, the calculated ^{18}O content of the tungstate at equilibrium was 1.27%; found, 1.30 ± 0.00%. Errors are standard deviations for from two to four replicate CO_2 samples. Results seem to indicate complete exchange in the time of mixing and separation, and the 3–7% enrichment of ^{18}O in the tungstate is probably real.[8]

In the experiments to check for oxygen exchange between water and 12-tungstocobaltate(III) and to determine whether or not it was rapid enough to be considered in the electron exchange between 12-tungstocobaltate(II) and -(III), the ^{18}O content calculated for no exchange was 0.206% (estimated from multiple analyses of natural water and Matheson "Bone Dry grade" CO_2). The ^{18}O content of the tetramethylammonium 12-tungstocobaltate(III) samples averaged 0.211 ± 0.002%). Complete exchange requires 1.49% ^{18}O. No appreciable oxygen exchange is indicated.

It seems safe to report that there is relatively rapid exchange (within a few minutes) of ^{18}O between water and orthotungstate at 25°, which might possibly be studied by simple stop-flow techniques. There seems to be no appreciable exchange of oxygen between water and 12-tungstocobaltate(III). The latter information tends to support our previous suggestion of an outer-sphere mechanism for the electron exchange between 12-tungstocobaltate(III) and -(II).[3]

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[8] J. Bigeleisen, private communication.

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Cyclic Heteroatomic Inorganic Compounds. A New Class of Phosphorus–Nitrogen–Boron Compounds

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A new class of cyclic compounds has been obtained which contains the elements phosphorus, nitrogen,

TABLE I

BORAPHOSPHONITRILE COMPOUNDS

No.	Compound	Yield, %	M.p.,[a] °C.	N, % Found	N, % Calcd.	P, % Found	P, % Calcd.	B, % Found	B, % Calcd.	X,[b] % Found	X,[b] % Calcd.
II	$[(C_6H_5)_4P_2N_3H_2BCl]BCl_4$	81	204	6.81	6.85	10.21	10.10	3.70	3.53	28.13	28.90
III	$[(C_6H_5)_4P_2N_3H_2B(C_6H_5)]B(C_6H_5)Cl_3$	75	>340	6.20	6.03	9.12	8.89	3.29	3.11	15.30	15.27
IV	$[(C_6H_5)_4P_2N_3H_2BBr]BBr_3Cl$	77	204	5.13	5.31	7.73	7.83	2.59	2.73	45.00	44.88
V	$[(C_6H_5)_4P_2N_3H_2BCl]Cl$	90	302–304	8.29	8.47	12.26	12.49	2.30	2.18	14.20	14.29
VI	$[(C_6H_5)_4P_2N_3H_2B(C_6H_5)]Cl$	70	323–325	7.61	7.81	11.37	11.52	1.94	2.01	6.96	6.59
VII	$[(C_6H_5)_4P_2N_3H_2BBr]Cl$	78	201 dec.	7.10	7.77	11.25	11.46	1.42	2.00	21.30	21.34
VIII	$(C_6H_5)_4P_2N_3HBCl$	79	304–306	8.93	9.14	12.93	13.48	2.67	2.35	7.34	7.71
IX	$(C_6H_5)_4P_2N_3HB(C_6H_5)$	80	210	8.14	8.38	12.49	12.36	1.96	2.16	0.00	0.00
X	$(C_6H_5)_4P_2N_3HBBr$	83	328–330	8.38	8.34	11.71	12.29	1.85	2.15	16.20	15.85

[a] All melting points are uncorrected for samples in open capillaries. [b] Total halogen.

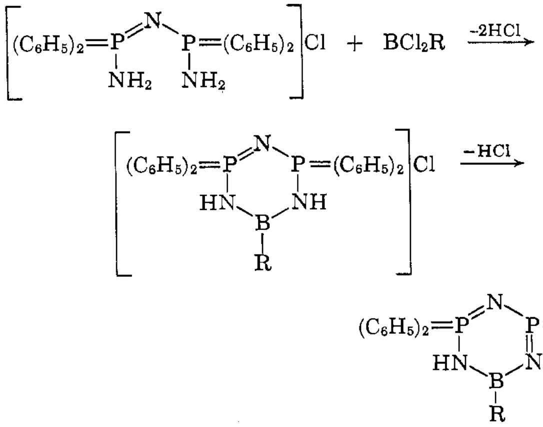
TABLE II

SELECTED INFRARED ABSORPTION BANDS FOR BORAPHOSPHONITRILE COMPOUNDS[a]

$[RbCl]$-BCl_4[b] II	$[RB(C_6H_5)]$-$B(C_6H_5)Cl_3$ III	$[RBBr]$-BBr_3Cl IV	$[RBCl]Cl$ V	$[RB$-$(C_6H_5)]Cl$ VI	$[RBBr]Cl$ VII	$R'BCl$[c] VIII	$R'B(C_6H_5)$ IX	$R'BBr$ X	Assignment
3280 m	3290 w	3250 m	3180 m	3160 m	3180 m	3180 m	3190 m	3175 m	NH str.
1390 s	1390 s	1370 s	1390 s	1370 m, sh	1395 m	1395 s	1395 s	1390 w	Ring B—N str.
1342 s	1345 s	1332 s	1333 m	1342 s	1328 s	1350 s	1340 s	1330 s	
1168 s	1240 s	1170 s	1200 m	1230 s	1230 s	1205 s	1183 s	1200 s	P=N—P str.
							1162 s		
1041 s	1030 m	1037 s							Tentatively assigned to N—H in-plane bend
1020 s	1018 m	1022 m	1024 s	1018 w	1020 s	1025 s	1023 m	1022 vs	
895 m	882 m	895 w							B—Cl str.
		878 m	858 w, br			862 w			
844 m			848 w						
770 m		770 m	775 m, br			767 m, br			
	695 s	695 s							
640–740 s, br									
	642 m	630 s	629 m		629 w	629 m		629 m	Unassigned

[a] Frequencies are given in wave numbers. [b] $R = (C_6H_5)_4P_2N_3H_2$. [c] $R' = (C_6H_5)_4P_2N_3H$.

and boron in the ring. The general method for the preparation of these compounds is given in the equation



where R = C_6H_5 or Cl. Boron tribromide was also used. This method utilizes a previously reported cyclization reaction.[1] 1-Amido-1,1,3,3-tetraphenyl-4,4-dihydridoketadiphosphonitrilium chloride (I) was first prepared by Bezman and Smalley[2] and its structure given by Sisler.[3] The yields, melting points, and elemental analyses of the boraphosphonitriles are given in Table I.

Pertinent infrared data and band assignments are given in Table II. All of the compounds (I–X) contain a single band in the region of 3290–3160 cm.$^{-1}$, which is assigned to the N–H stretching vibration, and a band in the 3075–3050 cm.$^{-1}$ region, which is the aromatic C–H stretching frequency. In addition they all contain bands in the regions of 1435–1445 and 965–992 cm.$^{-1}$ which are attributed to the P—C_{phenyl} bonds.[3] A band attributed to the P=N—P linkage was found in all of the boraphosphonitriles in the region of 1162–1240 cm.$^{-1}$. These bands appear below the frequency of 1250 cm.$^{-1}$ for the corresponding band in the spectrum of I. The ring B–N stretching vibrations in the 1328–1395 cm.$^{-1}$ region of the boraphosphonitriles lie close to the characteristic borazine ring stretching vibrations in the 1400 cm.$^{-1}$ region.[4] The medium-to-strong band at 1020–1025 cm.$^{-1}$, which is present in all of the boraphosphonitriles but not in compound I, falls close to the 1030 cm.$^{-1}$ band of borazine compounds. This band has been assigned to a normal frequency of the N–H bending mode in the molecular plane of the ring[5] coupled with the B–Cl stretch. It is tentatively assigned to the N–H in-plane bending mode in the boraphosphonitriles. The

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characteristic strong bands at 692–709 and 659–675 cm.$^{-1}$ of the tetrachloroborate ion[6,7] overlap with the C–H deformation frequencies in the 680–740 cm.$^{-1}$ region to give a very broad strong absorption from 640 to 740 cm.$^{-1}$.

The ring formulation for boraphosphonitriles is most reasonable in view of the strong tendency of boron-containing inorganic polymers to form small rings rather than long chain polymers.[8] Boron trihalides and phenylboron dichloride are known to react readily with diamines to form cyclic compounds.[9] A molecular weight of 459 (501 theoretical) was obtained for $(C_6H_5)_4P_2N_3HB(C_6H_5)$ (IX), which was measured with a vapor pressure osmometer on solutions of IX in chloroform (ethanol stabilizer not removed). The low molecular weight is probably due to a very slow reaction of IX with ethanol. Ethanol reacts to a greater or lesser extent with all of the boraphosphonitriles. Solubility of the boraphosphonitriles in ethanol-free chloroform was so low as to prevent molecular weight determinations. The solubilities of the boraphosphonitriles were too low in organic solvents in which reliable molecular weights could be measured and which were unreactive.

In a formalistic sense the cyclic boraphosphonitriles are composites of phosphonitriles and B-substituted borazines. Whereas the borazines contain boron–nitrogen bonds that are highly localized two-center π bonds,[10] the cyclic phosphonitriles are considered to have a certain degree of delocalization in the ring.[11,12] Ultraviolet spectra of chloroform solutions of the boraphosphonitriles down to 250 mμ showed no bands that could be assigned to a conjugated inorganic ring system, although such bands may exist below this wave length. The ultraviolet spectrum of I shows three bands at 261 mμ (ϵ 2400), 267 mμ (ϵ 2970), and 273 mμ (ϵ 2360) which are due to the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition mixed with the vibronic interaction. The $^1B_{1u} \leftarrow {}^1A_{1g}$ transition of the phenyl rings in I could be observed in acetonitrile solution at λ_{max} of 225 mμ. The spectrum of triphenylphosphine oxide in 95% ethanol also shows a well-defined vibrational structure characteristic of unperturbed or weakly perturbed phenyl rings at 260 mμ (ϵ 1520), 265.5 mμ (ϵ 1960), and 272.5 mμ (ϵ 1620), and the primary bands at 224.5 mμ (ϵ 2.14 × 10^4).[13] The positions of the $^1B_{2u} \leftarrow {}^1A_{1g}$ bands in the boraphosphonitriles are the same as in compound I. The intensities vary slightly. It is evident that the several P-phenyl rings in these compounds do not greatly perturb each other and thus are not appreciably conjugated with one another.

Experimental Section

Reagents.—Compound I was prepared from diphenyltrichlorophosphorane and ammonia gas according to the procedure described by Bezman and Smalley.[2] Technical grade diphenylchlorophosphine, which was used to prepare the phosphorane, was generously supplied by Victor Chemical Works and was used without further purification. Chlorine gas, ammonia, and boron trichloride were obtained from the Matheson Company and were used without further purification.

Phenyldichloroborane was prepared in good yields from tetraphenyltin (Fisher practical grade) and boron trichloride according to a previously reported procedure.[14]

The 1,2-dichloroethane used as solvent for the cyclization reactions was obtained from Eastman Kodak. It was shaken for 12 hr. with anhydrous potassium carbonate and then distilled.

Preparation of $[(C_6H_5)_4P_2N_3H_2BCl][BCl_4]$ (II).—In a typical reaction, a suspension of 2.26 g. (5.00 mmoles) of compound I in 50 ml. of dichloroethane was cooled to −5° in a salt–ice bath. Liquid boron trichloride was added in excess of 10.0 mmoles and the mixture was stirred under nitrogen until all of compound I dissolved. The reaction was permitted to proceed for several minutes and then the solvent plus HCl and excess boron trichloride were removed under reduced pressure at room temperature. The crystalline material that remained was washed with dry benzene in a closed system and recrystallized from dichloroethane. This compound reacts violently with water and alcohol with the formation of HCl and boric acid. It is sparingly soluble in tetrachloroethane.

Preparation of $[(C_6H_5)_4P_2N_3H_2B(C_6H_5)][C_6H_5BCl_3]$ (III).—To a suspension of 2.26 g. of I in 50 ml. of dichloroethane, 1.6 g. (10 mmoles) of phenyldichloroborane was added at room temperature. Compound I dissolved immediately with the evolution of HCl gas. The mixture was refluxed for 2 hr. Upon cooling, 2.5 g. of crude III separated. The compound was washed with *n*-pentane and recrystallized from a nitrobenzene–*n*-pentane solution. Compound III is difficultly soluble in chloroform, tetrachloroethane, and dichloroethane. It is insoluble in water and hydrolyzes only slowly. It is soluble in ethanol with apparent reaction as evidenced from the evolution of hydrogen chloride.

Preparation of $[(C_6H_5)_4P_2N_3H_2B\ Br][B\ BrCl_3]$ (IV).—This compound was prepared in a manner similar to that described for II.

Preparation of $[(C_6H_5)_4P_2N_3H_2BCl]Cl$ (V).—This compound may be prepared in either of two ways. By the first method compound II was pyrolyzed at 230° for 48 hr. under a reduced pressure of 2 mm. to give essentially quantitative yields of V. The compound is less reactive to hydrolysis than the tetrachloroborate.

The compound may also be prepared directly by allowing a 1:1 mole mixture of compound I and boron trichloride in dichloroethane to react at room temperature for about 1 hr. Because the reaction is highly exothermic, the boron trichloride was added slowly to the suspension of I in dichloroethane which had been cooled to 0° in an ice bath. The solvent was then removed under vacuum and the crude crystals of V recrystallized from dichloroethane.

Preparation of $[(C_6H_5)_4P_2N_3H_2B(C_6H_5)]Cl$ (VI).—This compound was prepared in a fashion similar to that described for III except the reagents were mixed in a 1:1 molar ratio. The crude product was recrystallized from dichloroethane–*n*-pentane.

Preparation of $[(C_6H_5)_4P_2N_3H_2BBr]Cl$ (VII).—This compound was prepared in a manner similar to the second method for preparing V. It was recrystallized from dichloroethane.

Preparation of $(C_6H_5)_4P_2N_3HBCl$ (VIII).—A suspension of 2.26 g. (5.00 mmoles) of I in 50 ml. of dichloroethane was mixed with 0.41 ml. (5.0 mmoles) of boron trichloride. The reaction

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