

TABLE II
 X-RAY POWDER DIFFRACTION DATA ON MgSiN₂

This work		David and Lang ¹	
Interplanar spacing, <i>d</i> , Å	Intens	Interplanar spacing, <i>d</i> , Å	Intens
4.07	14	4.08	Minor
3.94	15	3.94	Minor
3.33	17		
2.76	79	2.75	Very strong
2.63	55	2.65	Strong
2.49	86	2.49	Very strong
2.41	100	2.41	Very strong
2.33	29	2.33	Moderate
2.19	5		
2.105	6		
1.85	25	1.85	Moderate
1.81	13	1.81	Trace
1.615	20	1.614	Minor
1.576	26	1.543	Moderate
		1.404	Faint
1.377	6	1.379	Faint
1.356	13	1.356	Trace
1.328	9	1.329	Faint
1.312	17	1.312	Minor
		1.275	Very faint
1.247	5	1.246	Very faint
1.224	24		
1.207	8	1.207	Very faint
1.069	6		
1.061	23		
1.033	17		
1.001	15		
0.987	5		
0.984	5		
0.972	6		
0.970	12		
0.938	10		
0.931	9		
0.919	8		
0.892	9		
0.871	14		
0.862	13		
0.858	6		
0.829	7		
0.808	13		
0.796	7		

diffraction data on MgSiN₂ powder were obtained and compared with previously published results.

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Some Ring Expansion Reactions of Phosphorus and Boron Imidazolidines (1,3-Diaza-2-phospholidines and -borolidines)

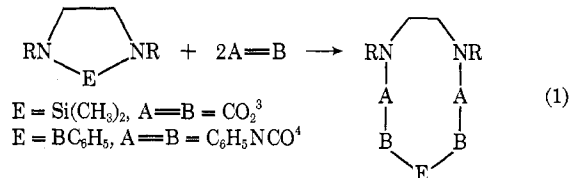
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Insertion reactions are especially significant in organometallic chemistry in providing easy syntheses

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of compounds containing functional groups.² Insertion of unsaturated substrates into the E-N bonds of silicon³ and boron imidazolidines⁴ has led to nine-membered, ring-expanded products



This paper reports several examples of the insertion reactions of boron and phosphorus imidazolidines.

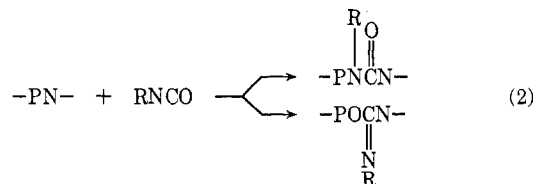
Results and Discussion

The reaction of methyl and phenyl isocyanates with 1,3-dimethyl-2-phenyl-1,3-diaza-2-phospholidine (phosphorus imidazolidine) on a millimole scale in benzene is exothermic and gives in each case a material containing 2 mol of the isocyanate with a strong absorption at *ca.* 1700 cm⁻¹ in the infrared region which could be due to either the C=O or C=N groups, depending on the mode of insertion (see Table I).

 TABLE I
 DATA FOR

A=B	Ratio	Form	Anal., %			
			Calcd		Found	
			C	H	C	H
E = PC ₆ H ₅						
CH ₃ NCO	1:2	Light yellow, low melting	54.53	6.82 ^b	52.77	6.82 ^b
C ₆ H ₅ NCO	1:2	Dark yellow oil	66.67	5.77	65.63	6.03
Cl ₃ CCHO	1:1	Brown oil	42.15	4.68	42.79	4.52
CS ₂	1:1	Red solid, mp 88-99°	48.89	5.65	50.69	6.22
E = BC ₆ H ₅						
Cl ₃ CCHO	1:2	Brown solid, mp 74-75°	35.95	3.52	36.88	3.98
C ₆ H ₅ NCS	1:1	White solid, mp 63-64°	66.00	6.51	66.05	6.57

^a Microanalyses were performed by Instranal Laboratory, Inc., Rensselaer, N. Y. ^b N: calcd, 18.18%; found, 18.3%.



By analogy with the findings of Lappert, *et al.*,⁵ and Hudson, *et al.*,⁶ we assume that the insertion of N=C had taken place to yield a nine-membered bis(ureido)-phenylphosphine ring as depicted in eq 1. The reaction of phenyl isocyanate with boron imidazolidine gives the analogous bis(ureido)borane.⁴

1,3-Dimethyl-2-phenyl-1,3-diaza-2-borolidine (boron imidazolidine) reacts with phenyl isothiocyanate to form

(2) M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, **5**, 225 (1967).

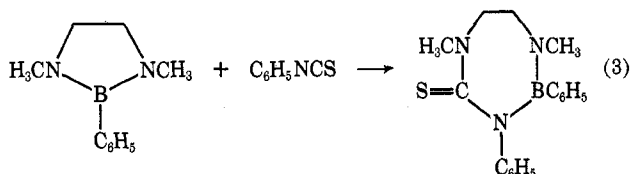
(3) C. H. Yoder and J. J. Zuckerman, *Chem. Commun.*, 694 (1966).

(4) R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.*, 2108 (1964).

(5) R. H. Cragg and M. F. Lappert, *ibid.*, 82 (1966).

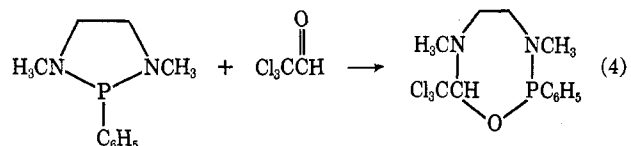
(6) R. F. Hudson and R. J. G. Searle, *Chem. Commun.*, 1249 (1967).

the 1:1 adduct in an exothermic reaction

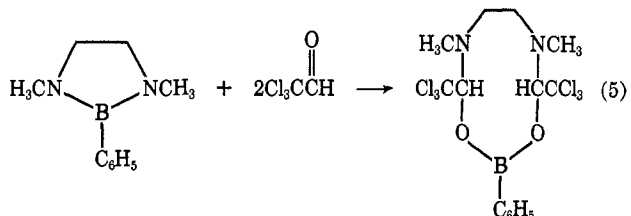


Presumably the insertion of 1 mol of the isothiocyanate deactivates the heterocycle for further insertion.

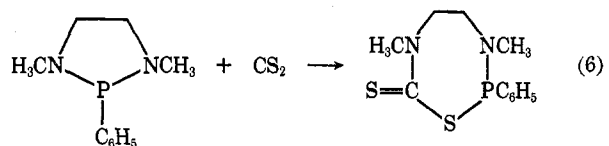
Chloral behaves similarly toward the phosphorus imidazolidine in benzene to give a 1:1 adduct in an exothermic reaction



With the boron heterocycle, on the other hand, 2 mol of chloral was taken up in an exothermic reaction



The addition of carbon disulfide to the phosphorus imidazolidine is highly exothermic and produces the 1:1 adduct as a blood red solid



A similar coloration was observed when bis(dimethylamino)phenylphosphine was treated with carbon disulfide.⁵

Our investigation shows that the reactivity of the boron and phosphorus imidazolidines toward insertion is in general similar but depends in the particular case on the inserting moiety.

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Raman Intensity of the A_1 Line and Bond Order of the Perbromate Ion

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The recent synthesis of the perbromate ion, BrO_4^- , by Appelman³ and Brown, *et al.*,⁴ has ended the need for

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(2) To whom correspondence should be addressed.

(3) E. H. Appelman, *Inorg. Chem.*, **8**, 223 (1969).

(4) L. C. Brown, G. M. Begun, and G. E. Boyd, *J. Amer. Chem. Soc.*, **91**, 2250 (1969).

attempts to explain the apparent nonexistence of this species. Included in past speculation about possible causes of the apparent instability of BrO_4^- are a number of theoretical considerations which have been summarized by Cox and Moore.⁵ One kind of experimental measurement involved in attempting to account for the history of failures to prepare the BrO_4^- ion is the Raman intensity of the A_1 line⁶ and later bond orders obtained from these Raman intensities.⁷ In view of general interest in the BrO_4^- ion and the role played by Raman intensities in an attempt to account for the apparent nonexistence of the BrO_4^- ion based on a possible low bond order for the Br–O bond,⁷ it now seemed appropriate to measure the Raman intensity of the A_1 line of the BrO_4^- ion and compare this intensity and resulting bond order to results for the ClO_4^- and IO_4^- ions.

Experimental Section

Chemicals.—Potassium perbromate was a gift from Dr. E. H. Appelman of Argonne National Laboratory. Reagent grade potassium perchlorate (Baker & Adamson) and potassium periodate (Fisher) were used as received.

Spectrometer.—Raman spectra were recorded on a system consisting of a Spex Model 1401 double monochromator equipped with a Coherent Radiation Laboratory Model 52 Ar ion laser source (~ 1.3 W at 5145 Å) and photon counting detection *via* an ITT FW-130 photomultiplier maintained at *ca.* -20° by a thermoelectric cooler (Products for Research, Inc.). The incident radiation from the laser was plane polarized and depolarization ratios were measured using the analyzer method recommended by Scherer and Bailey.⁸ A polarization scrambler was located between the analyzer and the entrance slit of the monochromator.

Intensity Measurements.—Raman intensities were measured using the ν_1 (A_1) line of the perchlorate ion as the internal standard following the procedure of Chantry and Plane.^{9,9} Observed depolarization ratios were indistinguishable from the expected value of zero for all three XO_4^- ions. Once this fact was established, the analyzer was removed from the optics to enhance the signal and attempt to improve the accuracy and reproducibility of band area measurements on the very dilute solutions employed. A total of fourteen measurements at two concentrations for perbromate and five measurements at one concentration for periodate were made, concentrations being *ca.* $(1-5) \times 10^{-3}$ M. Band areas were measured by planimeter.

Calculations.—For a tetrahedral molecule, the observed intensity for a totally symmetric (A_1) Raman line is given by¹⁰

$$I = \frac{KM(\nu_0 - \nu_1)^4 [45(\partial\bar{\alpha}/\partial Q_1)^2]}{\nu_1 [1 - \exp(-h\nu_1/kT)]} \quad (1)$$

where K is a constant, M is the molar concentration of the scattering species, ν_0 is the frequency of the exciting line, ν_1 is the frequency of normal coordinate Q_1 , $\bar{\alpha}$ is the mean molecular polarizability, and h , k , and T have their usual meanings. Since we wish to relate the measured intensity to bond properties, the

(5) M. M. Cox and J. W. Moore, *J. Phys. Chem.*, **74**, 627 (1970), and references therein.

(6) G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **34**, 1268 (1961).

(7) T. V. Long, II, and R. A. Plane, *ibid.*, **43**, 457 (1965).

(8) J. R. Scherer and G. F. Bailey, *Appl. Spectrosc.*, **24**, 259 (1970).

(9) G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **32**, 319 (1960).

(10) Combination of the equations for scattered intensity at 90° and depolarization ratio for plane-polarized incident radiation

$$I = \frac{KM(\nu_0 - \nu_1)^4 [45(\bar{\alpha}'_q)^2 + 7(\gamma'_q)^2]}{\nu_1 [1 - \exp(-h\nu_1/kT)]}$$

$$\rho = \frac{3(\gamma'_q)^2}{45(\bar{\alpha}'_q)^2 + 4(\gamma'_q)^2}$$

yields

$$I = \frac{KM(\nu_0 - \nu_1)^4 [45(\bar{\alpha}'_q)^2] \left[\frac{3(1 + \rho)}{3 - 4\rho} \right]}{\nu_1 [1 - \exp(-h\nu_1/kT)]}$$

Equation 1 is the special case of $\rho = 0$. All symbols are defined in the text except γ'_q the normal-coordinate derivative of the polarizability tensor anisotropy.