TABLE II

MAGNETIC DATA FOR [Fe(phen)$_2$X$_2$] AT 25°

X	μ_{eff}, B.M.
CN^-	0.74
Cl^-	5.26
Br^-	5.16
I^-	5.14
SCN^-	5.21

As expected, all of the halides are high spin, with the room temperature moment about that expected for a d^6 system. The previously reported values for bromide and iodide[2] are in error and probably arose, as has previously been suggested,[7] from the fact that under the conditions at which the bis compounds were supposedly prepared, a tris compound is merely dehydrated rather than converted to the bis.

The bis-thiocyanate is also observed to be high spin, as is indicated in Table II.

It is of interest to note that in attempting to prepare the bis-iodide by refluxing the tris-iodide in CCl_4, the moment of the sample rapidly changed to high spin values, but closer investigation showed that the high moment was due to the bis-chloride rather than the iodide, indicating a rapid exchange between the complex and solvent.

At the present time we are carrying out more extensive magnetic and spectral studies on these and related compounds. We also plan to investigate the nature of the halide exchange between the iodide and CCl_4.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Reaction of Borazine with Phenylmagnesium Bromide[1]

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The reaction of borazine[2] with phenylmagnesium bromide has never been reported. However, Smalley and Stafiej[3] have shown that the hydrogen atoms attached to boron in 1,3,5-trimethylborazine may be replaced by alkyl or aryl groups using Grignard reagents. It seemed likely that similar reactions would occur with the parent compound, borazine. Such reactions might offer a convenient synthetic approach to mono- and di-, alkyl and aryl, borazine derivatives substituted only on the boron atoms. The preparation of phenylborazine derivatives from borazine and phenylmagnesium bromide was therefore attempted. 2-Phenylborazine and 2,4-diphenylborazine were isolated and characterized. A small quantity of 2,4,6-triphenylborazine was also obtained.

Experimental

Materials.—Reagent grade solvents were dried over sodium wire before being used.

The borazine was prepared by the reduction of 2,4,6-trichloroborazine with sodium borohydride using the dimethyl ether of tetraethylene glycol as a solvent.[4]

A 3 *M* solution of phenylmagnesium bromide in ether was obtained from Arapahoe Special Products, Inc., of Boulder, Colorado. This solution was diluted with dry ether to one approximately 1 *M* in phenylmagnesium bromide and standardized.

Analytical Methods and Apparatus.—Carbon and hydrogen analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. All other analytical methods and apparatus were identical with those described in an earlier publication.[5]

Description of Experiment and Separation of the Products.—A 300-ml. flask, equipped with a magnetic stirrer and fitted with an addition funnel, was attached to a vacuum system. In a typical preparation 4.0 g. (0.05 mole) of borazine was distilled into the reaction flask from the vacuum system. Dry ether (175 ml.) followed by 48 ml. of 1.05 *M* phenylmagnesium bromide in ether (0.05 mole) were then added by means of the addition funnel. The addition of phenylmagnesium bromide was carried out over a 30-min. period with constant stirring. The resulting solution was allowed to stand at room temperature under an atmosphere of nitrogen overnight.

The flask was removed from the vacuum system and 50 ml. of dry cyclohexane was added to the reaction mixture. Ether was removed by distillation at atmospheric pressure and the resulting cyclohexane solution decanted from the solid that separated. The cyclohexane was removed from this solution by evaporation at room temperature on a vacuum system. About 6 g. of a fluffy white powder remained. This white powder was found to be a mixture of 2-phenylborazine, 2,4-diphenylborazine, 2,4,6-triphenylborazine, and some magnesium salts. It was possible to separate the three borazines by fractional sublimation.

The reaction residue was placed in a vacuum sublimator and fractions were collected at 40, 70, 100, 130, and 165°. Heating was continued for about 48 hr. at each temperature. Several grams of a nonvolatile white solid remained in the sublimator after 48 hr. at 165°. A solution of this material in water gave positive tests for bromine and magnesium.

The material collected at 40, 100, and 165° was, respectively, crude 2-phenylborazine, 2,4-diphenylborazine, and 2,4,6-triphenylborazine. The material collected at 70° was 2-phenylborazine containing some 2,4-diphenylborazine while the material collected at 130° was 2,4-diphenylborazine containing some 2,4,6-triphenylborazine. The crude 2-phenylborazine, 2,4-diphenylborazine, and 2,4,6-triphenylborazine were purified by repeated vacuum sublimations at 40, 100, and 165°, respectively. Purified 2-phenylborazine (1.5 g., 19% yield based on phenylmagnesium bromide), purified 2,4-diphenylborazine (0.9 g., 15% yield), and purified 2,4,6-triphenylborazine (0.2 g., 4% yield) were obtained.

Description.—Both 2-phenylborazine and 2,4-diphenylborazine form colorless crystals when sublimed. 2-Phenylborazine melts

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[1] Abstracted from a part of a Ph.D. thesis submitted by P. C. Moews' Jr., to the Department of Chemistry, Cornell University, 1960.

[2] In line with the recommendations of the Committee on the Nomenclature of Boron Compounds, the term borazine is used in this paper rather than the older term borazole. A numerical prefix precedes the name of the substituent and designates its location on the ring; numbering the ring begins with the nitrogen atom.

[3] J. H. Smalley and S. F. Stafiej, *J. Am. Chem. Soc.*, **81**, 582 (1959).

[4] L. F. Hohnstedt and D. T. Haworth, *ibid.*, **82**, 89 (1960).

[5] A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, *ibid.*, **83**, 1337 (1961).

at 73.5–75° while 2,4-diphenylborazine melts at 120–122°. 2,4,6-Triphenylborazine has already been described. It was identified by its melting point, 175–177° (reported 175–176°[6] and 183–185°[7]), and by its infrared spectrum.[6]

Anal. Calcd. for $B_3N_3C_6H_{10}$: B, 20.8; N, 26.8; C, 45.0; H, 6.43; active H for 2 B–H bonds per molecule, 1.27. Found: B, 20.4, 21.0; N, 26.0, 25.8; C, 48.8, 49.0; H, 6.36, 6.33; active H, 1.25.

Anal. Calcd. for $B_3N_3C_{12}H_{14}$: B, 14.0; N, 18.1; C, 61.9; H, 6.06. Found: B, 13.7; N, 17.9; C, 61.6; H, 6.16. The infrared spectra of samples of 2-phenylborazine and 2,4-diphenylborazine contained in KBr pellets are recorded in Table I and X-ray diffraction patterns of the two compounds are given in Table II.

TABLE I
INFRARED SPECTRA OF 2-PHENYLBORAZINE AND 2,4-DIPHENYLBORAZINE[a]

2-Phenylborazine		2,4-Diphenylborazine	
cm.$^{-1}$	I/I^0	cm.$^{-1}$	I/I^0
3470	m	3460	m
2500	m	2505	w
1600	m	1605	m
1500	sh	1510	m
1440	vs	1455	vs
1425	sh	1365	m
1375	m	1250	w
1335	m	1205	w
1220	w	909	m
1070	w	899	s
1000	w	772	w
895	s	708	s
769	w		
736	sh		
713	s		

[a] The symbols used to designate intensities are: s, strong; m, medium; w, weak; v, very; and sh, shoulder.

TABLE II
X-RAY POWDER PATTERNS OF 2-PHENYLBORAZINE AND 2,4-DIPHENYLBORAZINE[a]

2-Phenylborazine		2,4-Diphenylborazine	
d, Å.	I/I_0	*d*, Å.	I/I_0
10.2	m	6.21	vw
5.39	w	5.29	w
4.46	vs	4.91	m
3.97	s	4.54	vs
3.77	vw	4.11	s
3.38	vw	3.67	m
3.11	s	3.57	vw
3.08	vw	3.52	s
2.91	vw	2.89	vw
2.72	w	2.69	vw
2.60	w	2.21	vw
2.52	vw	1.97	vw
2.42	vw	1.82	vvw
2.36	vw	1.66	vvw
2.16	w		
2.08	w		
1.91	w		
1.70	w		

[a] The symbols used to designate intensities are: s, strong; m, medium; w, weak; and v, very.

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CONTRIBUTION FROM THE SPERRY RAND
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Solid Solution in the Gallium Arsenide–Indium Arsenide System

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The occurrence of solid solubility in binary systems of III–V semiconductor compounds has been studied by a number of investigators. Some of the early results suggested that only limited ranges of solid solution could be obtained in the systems GaSb–InSb, GaSb–AlSb, and InSb–AlSb.[1] Goryunova and Federova[2] reported that a lengthy annealing period in the solid state was necessary to achieve a single phase in the GaSb–InSb system, although this was not adequate for homogenization of GaAs–InAs compositions. Subsequently it has been shown[3–5] that for most of the binary III–V systems it is possible to prepare reasonably homogeneous single-phase material provided that a sufficiently prolonged heat-treatment of the powdered solid is used, at a temperature not far below the solidus level. The feasibility of preparing massive (unpowdered) homogeneous products was discussed by Woolley and Smith.[5] They applied both zone recrystallization and directional freezing to an equimolar GaSb–InSb composition but in each case obtained a spread of composition across any given cross section of the ingot. The gradient freezing and zone leveling methods, using a traveling furnace, were applied to the GaAs–InAs system by Abrahams, Braunstein, and Rosi.[6] The zone leveling technique gave greater homogeneity across a given section of an ingot, and they reported composition spreads of <2% near the ends of the phase diagram. Woolley, Gillett, and Evans[7] subsequently described the preparation of GaAs–InAs samples by the directional freezing technique over the range 11–82 mole % GaAs. Above 82 mole % GaAs, prolonged annealing of solidified melts was used.

It is important to note that in all the above investigations the resultant materials were essentially polycrystalline, quite apart from any question of homogeneity.

The work now reported was intended to investigate the possibility of preparing GaAs, containing a small percentage of InAs in solid solution, in the form of single crystals of a usable size from the standpoint of physical measurements.

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