TABLE V

HEAT AND ENTROPY OF ACTIVATION

	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	Temp. range	Ref.
$OCBH_3 \rightarrow BH_3 + CO$	10.2	28.4	327 to 337°K.	This paper
$BH_3 + CO \rightarrow OCBH_3$	−23.0	9.6	327 to 337°K.	This paper
$B_2H_6 \rightarrow BH_3 + BH_3$	....	28.4	....	Bauer[3]
$BH_3 + BH_3 \rightarrow B_2H_6$	....	0	....	Assumed by Bauer[3]

calculated to be −23.0 e.u. Table V summarizes the values of heat and entropy of activation.

A rough calculation indicates, at 60°, that the equilibrium constant for $OCBH_3 = BH_3 + CO$ is of the order of 10^{-5} (K_p, atm.), and that k_2 is approximately 1.6×10^3 atm.$^{-1}$ min.$^{-1}$. It is obvious that k_2 is much larger than k_1 and the decomposition of carbon monoxide borane to borane and carbon monoxide (eq. 1) is the slow step of the process.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, SCHENLEY PARK, PITTSBURGH 13, PENNSYLVANIA]

Phosphorus Nitrogen Chemistry. IV. The Reactions of Dimethylaminophosphines with Boron Trihalides and Trialkyls[1,2]

BY ROBERT R. HOLMES AND RAYMOND P. WAGNER[3]

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The reactions of $P[N(CH_3)_2]_3$, $CH_3P[N(CH_3)_2]_2$ and $(CH_3)_2PN(CH_3)_2$ with $B(CH_2CH_3)_3$, $B(CH_3)_3$, BF_3 and BCl_3 have been investigated. Evidence indicates that $B(CH_2CH_3)_3$ forms liquid 1:1 adducts at room temperature. $B(CH_3)_3$ forms solid 1:1 adducts at −46°. The reactions with BF_3, BCl_3 and excess $B(CH_3)_3$ were complex and slow. Analysis of the products yields $(CH_3)_2NBY_2$, where Y is CH_3, F or Cl, in all cases except the $P[N(CH_3)_2]_3$–$BCH_3)_3$ case. The data indicate that the reaction $(CH_3)_xP[N(CH_3)_2]_{3-x} + (3 - x)BY_3 \rightarrow (3 - x)(CH_3)_2NBY_2 + (CH_3)_xPY_{3-x}$ where x is 0, 1 or 2, proceeds to some extent in all cases, and over 75% in the $P[N(CH_3)_2]_3$-BF_3, $P[N(CH_3)_2]_3$-BCl_3 and $(CH_3)_2PN(CH_3)_2$–$B(CH_3)_3$ cases. Secondary reactions between $(CH_3)_xPY_{3-x}$ and the reactants led to an investigation of $(CH_3)PCl_2$ and $(CH_3)_2PCl$ with BCl_3. Solid 1:1 adducts were found at 0° which were slightly dissociated at room temperature. A possible reaction mechanism indicated by the data is considered.

Previously a study[4] of the thermal decomposition of borine adducts of $(CH_3)_2PN(CH_3)_2$ led to the production of N–B and P–B products. Working with trimethylborane and triethylborane, 1:1 adducts were formed in this study with the dimethylaminophosphines, $P[N(CH_3)_2]_3$, $CH_3P[N(CH_3)_2]_2$ and $(CH_3)_2PN(CH_3)_2$; however, in the case of the trimethylborane adducts and excess trimethylborane, further reaction ensued. Preliminary experiments showed that such reactions proceed much faster with boron trichloride in the initial stages as evidenced by the rapid take up of the gaseous trichloride by tris-dimethylaminophosphine. Fractionation of the product mixture in this case led to the isolation of dimethylaminoboron dichloride, phosphorus trichloride and small amounts of an oil.

To ascertain the variety and extent of the reactions occurring as well as correlate the behavior involved as far as possible, a more thorough investigation was conducted in which the reactions of the dimethylaminophosphine series with trimethylborane, boron trichloride and boron trifluoride were studied systematically.

Experimental and Results

Apparatus.—High vacuum systems equipped with mercury-float valves were used for part of this study. In general transfer operations outside the line and weighings were performed with the aid of a dry box. Samples of the phosphines, after purification in the vacuum line, were weighed without exposure to air directly into ampoules fitted with break tips and sealed and stored until ready for use. A special "reaction section" previously described[5] was used to study pressure-composition diagrams and to carry out the reactions in the systems described below.

In all tables reporting pressure–composition data, the mole fractions refer to condensed phase values. All ratios of quantities referred to in reaction mixtures are given in terms of moles.

Materials.—The purification of tank boron trifluoride and trichloride (Matheson) was described previously.[6] Vapor pressures of boron trifluoride samples at −111.7° were 297 mm. and for boron trichloride, 477 mm. at 0°.

Trimethylborane was prepared by a method described by Brown.[7] After fractionation the vapor pressure at −78.5° was 30.6 mm. (literature value,[8] 32 mm. at −78.4°).

Triethylborane (Callery Chemical Co.) was fractionated just prior to its use since increases in pressure were noted on storing.[8] The fractionated material exhibited a vapor pressure of 12.2 mm. at 0° (literature value[7,8] 12.4 mm., 12.5 mm. at 0°). The pressure would rise to about 16 mm. at 0° after 24 hr. and to as high as 40 mm. at 0° after a month of storage at room temperature.[8]

Tris-dimethylaminophosphine, $P[N(CH_3)_2]_3$, was prepared by the dimethylamine reaction with phosphorus trichloride in ether solution, similar to that described by Burg and Slota.[9] After distillation and fractionation in the line using −8°, −78° and −196° traps, the −8° trap contained the product having a vapor pressure of 2.2 mm. at 20° (literature,[9] 2.8 mm. at 20°) and a boiling point of 161° at 736.4 mm. (literature,[9] 163.5 at 760 mm.).

Dimethylaminodimethylphosphine, $(CH_3)_2PN(CH_3)_2$, was prepared and fractionated according to the procedure of Burg and Slota.[9] Vapor pressure at 0° was 12.2 mm. (literature,[9] 12.53 mm. at 0°).

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[1] Previous paper in the series: R. R. Holmes, *J. Am. Chem. Soc.*, **83**, 1334 (1961). Presented before the Inorganic Division at the 140th Meeting of the American Chemical Society, Chicago, Illinois, September, 1961.

[2] This paper represents part of the work submitted by Raymond P. Wagner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

[3] Research assistant (1959–1961). National Science Foundation Grant.

[4] A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **82**, 2145 (1960).

[5] H. C. Brown, L. P. Eddy and R. Wong, *ibid.*, **75**, 6275 (1953).

[6] H. C. Brown and R. R. Holmes, *ibid.*, **78**, 2173 (1956).

[7] H. C. Brown, *ibid.*, **67**, 374 (1945).

[8] A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921). These authors observed similar behavior and showed that small amounts of C_2H_6 and H_2 were produced.

[9] A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

Methyldichlorophosphine was generously donated by the Food, Machinery and Chemicals Corporation. About 50 ml. was distilled in a simple apparatus under a dry nitrogen atmosphere. It was further fractionated in the line by allowing the vapors to escape from a −42° trap and pass through traps cooled to −60°, −78° and −196°. The sample mostly in the −60° trap was tensiometrically homogeneous and had a vapor pressure of 25.5 mm. at 0°. However, after as little as one day the vapor pressure would rise a few mm. Hence, the compound was fractionated just prior to use.

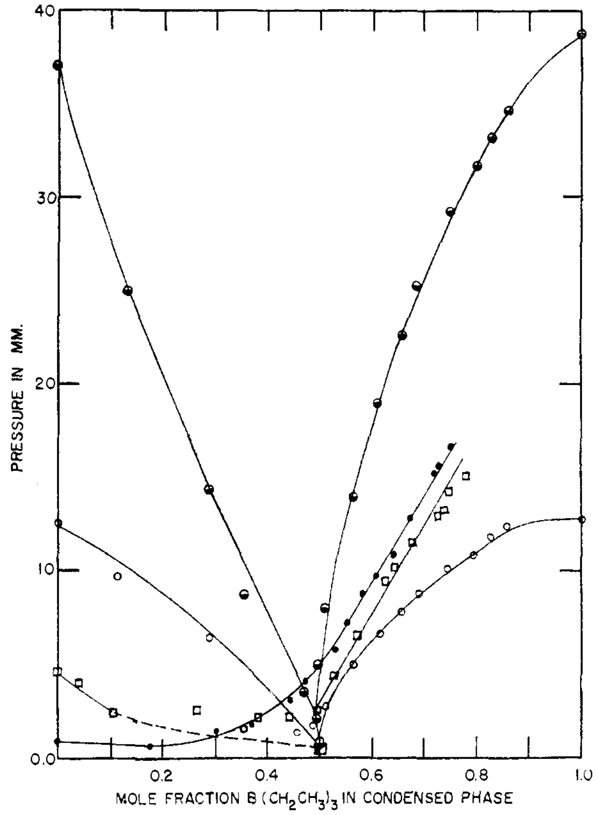

Fig. 1.—Pressure–composition studies of dimethylaminomethylphosphines and triethylborane: ●, $P[N(CH_3)_2]_3$-$B(CH_2CH_3)_3$ at 0°; □, $CH_3P[N(CH_3)_2]_2$-$B(CH_2CH_3)_3$ at 0°; ○, $(CH_3)_2PN(CH_3)_2$-$B(CH_2CH_3)_3$ at 0°; ◒, $(CH_3)_2PN(CH_3)_2$-$B(CH_2CH_3)_3$ at 20.0°.

Preparation of Bis-dimethylaminomethylphosphine.—$CH_3P[N(CH_3)_2]_2$, absent from the previous literature, was prepared by the reaction of methyldichlorophosphine, CH_3PCl_2, and dimethylamine in the vacuum line. $(CH_3)_2NH$, generated from the hydrochloride, passed over BaO and condensed on sodium chips (v.p., 566 mm. at 0°), was measured out in excess (44.26 mmoles) and condensed on 9.46 mmoles of CH_3PCl_2 at −196°. The reaction was allowed to proceed at −23°. A Dry Ice cone was used on the upper part of the reaction ampoule to cause the amine to reflux. After 2 hr. the contents were cooled to −78° and stored for 24 hr. The aminophosphine product and excess amine were transferred and fractionated (0°, −78°, −196° traps), leaving the hydrochloride behind. The excess amine separated showed an over-all reaction mole ratio of amine to CH_3PCl_2 of 3.9:1 (4.0:1 expected for 100% yield). The clear liquid in the −78° trap was further fractionated (0°, −23°, −78°, −196° traps). The −23° trap caught the bulk of the product and was tensiometrically homogeneous. Vapor pressures were 1.2 mm. at 0.1°, 1.8 mm. at 5.0°, 2.7 mm. at 10.0°, 3.7 mm. at 15.0°, 5.5 mm. at 20.0°; b.p., 141° at 755 mm.; m.p., −52° (float method).

Anal. Calcd. for $(CH_3)P[N(CH_3)_2]_2$: C, 44.76; H, 11.27: Found: C, 45.03; H, 11.15.

Experimental and Results

Dimethylaminophosphine Adducts with Triethylborane.—The results (Fig. 1) of pressure–composition studies of the systems, $P[N(CH_3)_2]_3$–$B(CH_2CH_3)_3$ at 0°, $CH_3P[N(CH_3)_2]_2$–$B(CH_2CH_3)_3$ at 0° and the $(CH_3)_2PN(CH_3)_2$–$B(CH_2CH_3)_3$ at 0° and 20°, indicate the formation of liquid 1:1 adducts at least in the latter two systems. The $P[N(CH_3)_2]_3$–$B(CH_2CH_3)_3$ system shows extensive dissociation. The vapor pressure of $B(CH_2CH_3)_3$ at 0.0° was 12.6 mm. and at 20.0°, 38.7 mm.

Values of the vapor pressures of the 1:1 adducts (except for the $P[N(CH_3)_2]_3$ adduct) were obtained on independent samples prepared by mixing equivalent amounts of the components. They are 0.2 mm. at 0.0° for $CH_3P[N(CH_3)_2]_2 \cdot B(CH_2CH_3)_3$, 0.4 mm. at 0.0° and 2.2 mm. at 20.0° for $(CH_3)_2PN(CH_3)_2 \cdot B(CH_2CH_3)_3$. These values were used in constructing Fig. 1. The latter was necessary since the values obtained in the pressure-composition determinations may be slightly high, the determination taking several hours during which the $B(CH_2CH_3)_3$ pressure slowly rises apparently giving small amounts of inert gaseous impurities. The latter effect was particularly noticeable in the study of the $CH_3P[N(CH_3)_2]_2$–$B(CH_2CH_3)_3$ system.

Dimethylaminophosphine Adducts with Trimethylborane. Pressure–composition studies were made on all three aminophosphine systems with trimethylborane at −46.0°. Representative data is shown for the $(CH_3)_2PN(CH_3)_2$–$B(CH_3)_3$ system in Table I. The slow rise in pressure in each case to a 1:1 mole ratio followed by a large increase in slope with further additions serves to indicate 1:1 adduct formation. The phase present at this point was a slightly wet white solid in each case at −46°. On warming to room temperature, the 1:1 adducts became liquid; however, the diagrams here may be complicated by further slow reaction with excess trimethylborane as discussed below.

TABLE I

THE DIMETHYLAMINODIMETHYLPHOSPHINE–TRIMETHYLBORANE SYSTEM AT −46.0°

Mole fraction, $B(CH_3)_3$ condensed phase	Press., mm.	Mole fraction, $B(CH_3)_3$ condensed phase	Press., mm.
0.066	1.1	0.512	78.4
.155	2.1	.538	132.2
.276	3.9	.584	187.5
.344	6.3	.639	210.8
.402	9.8	.703	202.9
.462	9.3	.784	209.4
.480	32.7		

In any event efforts to obtain equilibrium pressure–composition diagrams were not pursued at this time. Instead the slow reactions were studied in sealed ampoules which were allowed to remain at room temperature for varying lengths of time, after which the ampoules were opened in the vacuum line and the contents fractionated and analyzed.

The data on the sealed tube reactions are summarized in Table II. The number of mmoles of reactants in the sealed ampoules is shown (column two) as well as the mmoles of products formed where determined (column five). The per cent. yield is based on the amount of product formed according to the equation,

$$(CH_3)_xP[N(CH_3)_2]_{3-x} + (3 - x)BY_3 = (3 - x)(CH_3)_2NBY_2 + (CH_3)_xPY_{3-x}$$

where x is 0, 1 or 2 and Y is a halogen atom or a methyl group. Column four shows the moles of BY_3 consumed per mole of phosphine, the latter being determined by fractionating the unreacted BY_3 from the products and establishing its identity by vapor pressure measurements. Pertinent details for each system are discussed below.

Aminophosphine Reactions with Trimethylborane.—The reaction of $(CH_3)_2PN(CH_3)_2$ with $B(CH_3)_3$ was straight forward yielding $(CH_3)_2NB(CH_3)_2$ and $(CH_3)_3PB(CH_3)_3$ as the only isolatable products, the former identified by vapor pressure, molecular weight and analysis.

Temp., °C.	−45.2	−21.8	−15.0	−10.0	0	15.0	19.8
Press., mm.	3.1	16.2	23.3	31.1	53.6	114.8	139.2
Press., mm. (calcd.)[10]	2.8	14.7	22.5	30.2	52.6	111.1	135.8

TABLE II

SUMMARY OF THE REACTIONS OF THE DIMETHYLAMINOPHOSPHINES

Expt.[a] no.	Reactants (mmole)	Time, days	Reaction mole ratio	Products (mmole)	Yield, %
1	$P[N(CH_3)_2]_3 + B(CH_3)_3$ 2.48 10.36	30	0.96	$C_{10.0}H_{28.6}N_{3.33}P_{1.00}B_{2.00}$ (l) Uncharacterized solid	
2	$CH_3P[N(CH_3)_2]_2 + B(CH_3)_3$ 1.24 11.55	58	1.07	$(CH_3)_2NB(CH_3)_2$(l) 0.31 $C_{7.78}H_{26.14}N_{3.45}P_{1.00}B_{2.11}$ (l) Uncharacterized solid	12.5
3	$(CH_3)_2PN(CH_3)_2 + B(CH_3)_3$ 1.89 7.75	77	1.82	$(CH_3)_2NB(CH_3)_2$ (l) 1.48 $(CH_3)_3PB(CH_3)_3$ (s)	78.3
4	$P[N(CH_3)_2]_3 + BF_3$ 2.22 8.68	40	3.63	PF_3 (g) 2.02 $(CH_3)_2NBF_2$ (s) Yellow oil	91.0
5	$CH_3P[N(CH_3)_2]_2 + BF_3$ 3.02 6.37	19	1.91	$(CH_3)_2NBF_2$ (s) 1.68 Viscous liquid	27.8
6	$(CH_3)_2PN(CH_3)_2 + BF_3$ 3.88 15.87	120	1.73	$(CH_3)_2NBF_2$ (s) $C_{5.3}H_{18.4}N_{1.0}P_{1.9}B_{1.0}F_{7.5}$ (s) Uncharacterized viscous liquid	
7	$P[N(CH_3)_2]_3 + BCl_3$ 7.92 29.13	8	3.08	PCl_3 (l) 7.33 $[(CH_3)_2NBCl_2]_2$ (s) 10.7	92.7 90.1
8	$CH_3P[N(CH_3)_2]_2 + BCl_3$ 6.01 24.66	109	3.23	CH_3PCl_2 (l) $[(CH_3)_2NBCl_2]_2$ (s) $CH_3PCl_2 \cdot BCl_3$ (s)[b]	
9	$(CH_3)_2PN(CH_3)_2 + BCl_3$ 2.46 9.92	33	2.08	$[(CH_3)_2NBCl_2]_2$ (s) $(CH_3)_2PCl \cdot BCl_3$ (s)[b]	

[a] All experiments were conducted at room temperature except no. 7 (studied at 0°). [b] Product indicated.

Anal. Calcd. for $(CH_3)_2NB(CH_3)_2$: C, 56.54; H, 14.24; N, 16.49. Found: C, 56.33; H, 14.02; N, 16.24. Molecular weight (vapor density), 85.5 (calcd., 84.97).

The $(CH_3)_3PB(CH_3)_3$ was identified by vapor pressure, 1.94 mm. at 26.5° (Sujishi[11] reports 1.86 mm. at 30.0°), and analysis.

Anal. Calcd. for $(CH_3)_3PB(CH_3)_3$: C, 54.59; H, 13.74; P, 23.47; B, 8.20. Found: C, 54.25; H, 13.35; P, 23.28; B, 8.49.

The data illustrate the following slow reaction occurring

$$(CH_3)_2PN(CH_3)_2 + 2B(CH_3)_3 \longrightarrow (CH_3)_3PB(CH_3)_3 + (CH_3)_2NB(CH_3)_2$$

The reactions of $B(CH_3)_3$ with $CH_3P[N(CH_3)_2]_2$ and $P[N(CH_3)_2]_3$ were more complex yielding in each case a colorless liquid and an uncharacterized, non-volatile white solid. In addition a small amount of $(CH_3)_2NB(CH_3)_2$ was isolated from the $CH_3P[N(CH_3)_2]_2$ reaction (vapor pressure, 3.5 mm. at −45.0° and 33 mm. at −9.0°), but it was not searched for properly among the products of the $P[N(CH_3)_2]_3$ reaction with $B(CH_3)_3$.

Analysis of the liquid from the $CH_3P[N(CH_3)_2]_2$ reaction gave these results: *Anal.* C, 42.23; H, 11.91; N, 21.86; P, 14.00; B, 10.32. The total is 100.32% and gives a calculated empirical formula, $C_{7.78}H_{26.14}N_{3.45}P_{1.00}B_{2.11}$. A similar analysis was obtained for the liquid from the $P[N(CH_3)_2]_3$ reaction. *Anal.* C, 48.05; H, 11.57; N, 18.71; P, 12.42; B, 8.64, totaling 99.39%. The calculated formula is $C_{10.00}H_{28.60}N_{3.33}P_{1.00}B_{2.00}$. The formulas, however, do not lend themselves toward facile interpretation.

Aminophosphine Reactions with Boron Trifluoride. Table II shows that $(CH_3)_2NBF_2$ was isolated from each of the aminophosphine reactions with BF_3; however, in the case of $CH_3P[N(CH_3)_2]_2$ and $(CH_3)_2PN(CH_3)_2$ further analysis was complicated by the presence of viscous liquid products. The pertinent features of these reactions are discussed.

In the $P[N(CH_3)_2]_3$ reaction the gases pumped off consisted of a mixture of excess BF_3 and PF_3. Pyridine proved effective in separating the gases by forming a stable complex with BF_3[6], the PF_3 being unaffected. The gas mixture was bubbled through pyridine in a small U-trap cooled to −30°. A Dry Ice cone on the low pressure arm of the trap prevented pyridine from escaping. PF_3 was identified by its vapor pressure of 370.1 mm. at −111.7° and 187.6 mm. at −119° and molecular weight, 88.4 (calcd., 87.97).

The solid present was sublimed to a region on the stem of the ampoule which was cooled with a Dry Ice cone by heating the ampoule to 40°. Analysis of the solid showed it to be $(CH_3)_2NBF_2$, first described by Brown[12] and later more fully by Burg and Banus.[10] A yellow oil remained.

Anal. Calcd. for $(CH_3)_2NBF_2$: C, 25.86; H, 6.51; N, 15.08; B, 11.65; F, 40.91. Found: C, 25.61; H, 6.69; N, 15.07; B, 11.83; F, 40.76.

In the $CH_3P[N(CH_3)_2]_2$ reaction the solid $(CH_3)_2NBF_2$ was isolated by sublimation from the reaction mixture, the latter being heated toward 100° to complete the separation. The solid was trapped by a Dry Ice cone placed on the upper stem of the ampoule. Excess BF_3 passed through and was fractionated and measured. The water insoluble $(CH_3)_2NBF_2$ was cut off, weighed and analyzed.

Anal. Calcd. for $(CH_3)_2NBF_2$: N, 15.08; F, 40.91. Found: N, 15.31; F, 40.58.

The remaining liquid was caused to reflux at 140°; however, it was so viscous that it remained on the walls of the ampoule behaving more like a glassy solid. Continuing the heating to 200° caused small additional amounts of BF_3 and $(CH_3)_2NBF_2$ to be driven off.

The reaction of BF_3 with $(CH_3)_2PN(CH_3)_2$ behaved analogously to the $CH_3P[N(CH_3)_2]_2$ reaction, producing a viscous liquid and a solid. The latter was separated as before by sublimation at 100° but only a small amount (0.36 g.) isolated. It was insoluble in water and soluble in boiling water, characteristic of $(CH_3)_2NBF_2$.[12] A fluorine analysis was low (Calcd.: F, 40.91. Found: F, 37.79); however, considerable difficulty was experienced in separation.

A yellow solid remaining was separated from the viscous liquid by inverting the ampoule after resealing and placing its stub in a −196° bath. The liquid was transferred and the solid removed and analyzed.

Anal. C, 20.76; H, 6.06; N, 4.57; P, 18.83; B, 3.66; F, 46.50. The analyses totaled 100.38% and corresponded to the empirical formula, $C_{5.3}H_{18.4}N_{1.0}P_{1.9}B_{1.0}F_{7.5}$.

Along with the formation of $(CH_3)_2NBF_2$, CH_3PF_2 in some form is expected as a product of the reaction of $CH_3P[N(CH_3)_2]_2$ with BF_3. The compound CH_3PF_2 has been reported recently[13] and shows a b.p. of −28°; however,

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(10) Calculated from the equation of A. B. Burg and J. Banus, *J. Am. Chem. Soc.*, **76**, 3903 (1954).

(11) S. Sujishi, Ph.D. Thesis, Purdue University, 1949.

(12) J. F. Brown, *J. Am. Chem. Soc.*, **74**, 1219 (1952).

(13) V. N. Kulakova, V. M. Zinov'yev and L. Z. Soborovsikiy, *Zhur. Obshchei Khim.*, **29**, 3957 (1959).

a search for it proved fruitless. Indications are then that the viscous liquid produced in the $CH_3P[N(CH_3)_2]_2$ reaction may contain some complex or complexes of CH_3PF_2 such as $CH_3PF_2 \cdot BF_3$ or $CH_3PF_2 \cdot CH_3P[N(CH_3)_2]_2$.

Similarly the solid, $C_{5.3}H_{18.4}N_{1.0}P_{1.9}B_{1.0}F_{7.5}$, and viscous liquid from the $(CH_3)_2PN(CH_3)_2$ reaction may contain $(CH_3)_2PF$ in some form. The latter compound has not yet been described in the literature although F. Seel and coworkers[14] claim it can be prepared from $(CH_3)_2PCl$ using KSO_2F; however, they give no indication of having actually prepared it. Possibly by using stronger Lewis bases such as $(CH_3)_3P$, the fluoromethylphosphines could be displaced.

Aminophosphine Reactions with Boron Trichloride.—The initial reaction of $P[N(CH_3)_2]_3$ and BCl_3 was much more rapid than the corresponding reaction with $B(CH_3)_3$ as shown by preliminary pressure–composition studies. At 0° BCl_3 is taken up rapidly forming a solid with a slow rise in pressure to a 3:1 mole ratio. Afterwards, the pressure increases sharply with each further addition and the system becomes liquid-solid. At −46° the change in slope at 3:1 is much more distinct and the pressure rises, thereafter, to the vapor pressure of pure BCl_3.

In one run carried out at 0° (Table II) the contents of the ampoule were analyzed. The quantitative separation proved tedious and the details are given elsewhere.[15] All volatile products were transferred out of the ampoule at room temperature leaving a white solid and a small amount of a green oil. The unreacted BCl_3 was separated by collecting it in a −196° trap. All other volatile products were trapped at −78°. On standing solid formed in the −78° trap which proved to be a result of liquid $(CH_3)_2NBCl_2$ dimerizing. The latter combined with the white solid remaining in the ampoule (also dimeric $(CH_3)_2NBCl_2$ which was separated from the small amount of oil with CCl_4) was analyzed: m.p. 138–141° (literature value,[16] 142°). Brown and Osthoff[16] previously established the dimer formulation for the solid on the basis of molecular weight and dipole moment measurements.

Anal. Calcd. for $[(CH_3)_2NBCl_2]_2$: C, 19.09; H, 4.81; N, 11.13. Found: C, 19.08; H, 4.84; N, 11.08.

The liquid remaining in the −78° trap, after refractionation, was tensiometrically homogeneous, and its vapor pressure curve closely followed that of PCl_3. The molecular weight was determined (vapor density), 137.7 (calcd. for PCl_3, 137.3), normal b.p., 75–76° (PCl_3, 74.2°). The over-all reaction corresponded closely to

$$P[N(CH_3)_2]_3 + 3BCl_3 \longrightarrow PCl_3 + \frac{3}{2}[(CH_3)_2NBCl_2]_2$$

The reactions of $CH_3P[N(CH_3)_2]_2$ and $(CH_3)_2PN(CH_3)_2$ with BCl_3 proceeded similarly producing $[(CH_3)_2NBCl_2]_2$ in each case and suspected BCl_3 adducts with methylchlorophosphines (Table II). The amounts of products, however, were not determined. Product identifications in each system were made as follows:

In the $CH_3P[N(CH_3)_2]_2$ reaction, in addition to unreacted BCl_3, the volatile fraction contained CH_3PCl_2, vapor pressure, 25.8 mm. at 0.0°.

Anal. Calcd. for CH_3PCl_2: C, 10.27; H, 2.59; Cl, 60.65. Found: C, 10.57; H, 2.75; Cl, 60.36.

It was suspected that CH_3PCl_2 and BCl_3 were associating as noticed by a drop in pressure when the separated CH_3PCl_2 and BCl_3 were added together. The over-all ratio of 3.23 to 1 is higher than expected indicating some BCl_3 to be tied up with CH_3PCl_2. The existence of $CH_3PCl_2 \cdot BCl_3$ was substantiated by studying the system at 0°. A 1:1 white solid was clearly shown (a solid–liquid plateau present, 24 mm., followed by a sharp rise in pressure at 1:1).

The solid remaining in the ampoule was washed out with distilled water, filtered, dried and analyzed to be $[(CH_3)_2NBCl_2]_2$.

Anal. Calcd. for $[(CH_3)_2NBCl_2]_2$: N, 11.13; Cl, 56.37. Found: N, 11.07; Cl, 56.34.

The data obtained indicate the reaction

$$CH_3P[N(CH_3)_2]_2 + 3BCl_3 \longrightarrow CH_3PCl_2 \cdot BCl_3 + [(CH_3)_2NBCl_2]_2$$

After recovery of unreacted BCl_3 in the $(CH_3)_2PN(CH_3)_2$ reaction there remained a mixture of solids in the ampoule. Treating the mixture with 5% NaOH solution produced some solution. The insoluble fraction was filtered, washed and dried. Analysis showed it to be $[(CH_3)_2NBCl_2]_2$.

Anal. Calcd. for $(CH_3)_2NBCl_2$: C, 19.09; H, 4.81; N, 11.13; Cl, 56.37; B, 8.60. Found: C, 19.90; H, 4.98, N, 10.82; Cl, 55.67; B, 8.73.

The solid portion, soluble in 5% NaOH, was suspected to be $(CH_3)_2PCl \cdot BCl_3$. A pressure–composition study of the latter system at 0° showed the existence of a 1:1 adduct similar to that described for $CH_3PCl_2 \cdot BCl_3$. The adduct was soluble in 5% NaOH. The $(CH_3)_2PCl$ for the latter study was prepared according to the procedure of Burg and Slota.[9] The latter authors have found $(CH_3)_2PCl$ to react vigorously with $(CH_3)_2PN(CH_3)_2$ to form a nonvolatile adduct, $(CH_3)_2NP(CH_3)_2(CH_3)_2PCl$.[9] This fact shows that either the initial reaction between $(CH_3)_2PN(CH_3)_2$ and BCl_3 is sufficiently fast forming some intermediate before the production of $(CH_3)_2PCl$ so as not to permit the formation of $(CH_3)_2NP(CH_3)_2(CH_3)_2PCl$ or that the $(CH_3)_2PCl$ adduct with BCl_3 is more stable than $(CH_3)_2NP(CH_3)_2(CH_3)_2PCl$. Another possibility is the displacement of $(CH_3)_2PCl$ from $(CH_3)_2NP(CH_3)_2(CH_3)_2PCl$ by BCl_3.

Discussion

In general the dimethylaminophosphines can be said to react according to the equation

$$(CH_3)_xP[N(CH_3)_2]_{3-x} + (3\text{-}x)BY_3 \longrightarrow (CH_3)_2NBY_2 + (CH_3)_xPY_{3-x} \text{ where Y is } -CH_3, \text{ F or Cl}$$

Except for the $P[N(CH_3)_2]_3$–BF_3, $P[N(CH_3)_2]_3$–BCl_3 and $(CH_3)_2PN(CH_3)_2$–$B(CH_3)_3$ cases, there are many and varied side and competing reactions. Such reactions as those between BY_3 and $(CH_3)_2NBY_2$, BY_3 and $(CH_3)_xPY_{(3-x)}$, $(CH_3)_2NBY_2$ and $(CH_3)_xPY_{(3-x)}$, and $(CH_3)_xPY_{(3-x)}$ with $(CH_3)_xP[N(CH_3)_2]_{3-x}$ will have to be characterized in separate studies before the dimethylaminophosphine reactions can be fully understood.

Possible Course of the Reaction.—Burg and Banus[10] have studied the formation and decomposition of $(CH_3)_2NB(CH_3)_2BF_3$. In this adduct the most probable structure is a N–BF_3 linkage since no other electron pair donors are available. The products of decomposition were almost exclusively $(CH_3)_2BF$ and $(CH_3)_2NBF_2$ suggesting a fluoride-shift reaction. Fluoride shifts were also found in the $[(CH_3)_2N]_3SiH$–BF_3 reaction which gave $HSiF_3$.[17] The Si–H group is isoelectronic with phosphorus but has no unshared electron pairs. Here again BF_3 attack at nitrogen is reasonable with fluorides migrating to SiH.

The aminophosphines are seen to have two possible sites for attack, nitrogen and phosphorus. At present insufficient data is available to decide the point of initial attack by a boron halide or alkyl;[18] however, the over-all reactions proceed

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[14] F. Seel, H. Jonas, L. Riehl and J. Langer, *Angew. Chem.*, **67**, 32 (1955).

[15] R. P. Wagner, Ph.D. Thesis, Carnegie Institute of Technology, 1961.

[16] C. A. Brown and R. C. Osthoff, *J. Am. Chem. Soc.*, **74**, 2340 (1952).

[17] A. B. Burg, "Fluorine Chemistry," J. H. Simons, ed., Academic Press, Inc., New York, N. Y., 1950, p. 109.

[18] However, previous work has indicated P–B bonding to be preferred in diborane complexes. Thus X-ray *information is consistent* with the formulation $(NH_2)_3P \cdot BH_3$.[19] Indirect evidence[20] has been used to infer P–B bonding in $[N(CH_3)_2]_3P \cdot BH_3$. In $(CH_3)_2PN(CH_3)_2(BH_3)_2$[4], thermal decomposition yields products consistent with the formation of P–B bonding at some point as well as N–B bonding.

[19] C. E. Nordman, *Acta Cryst.*, **13**, 535 (1960).

[20] T. Reetz and B. Katlafsky, *J. Am. Chem. Soc.*, **82**, 5036 (1960).

analogously to those described above. At some point a N–B bond is formed and either halogen migration or methyl migration occurs to give the products, $(CH_3)_2NBY_2$ and $(CH_3)_xPY_{3-x}$.

In the aminophosphine reactions with $B(CH_3)_3$ 1:1 adducts may serve as initial steps. Studies at −46° showed that such adducts were isolatable with additional reaction proceeding very slowly; however, no adducts were obtained with the boron halides apparently due to the much higher reactivity encountered.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS]

The Preparation of Organolithium Compounds by the Transmetalation Reaction. IV. Some Factors Affecting the Transmetalation Reaction[1]

BY DIETMAR SEYFERTH AND MICHAEL A. WEINER

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Evidence is presented to show that the exchange reaction occurring between organolithium compounds and allyl- and vinyltin compounds is an equilibrium reaction. The position of the C=C bond in olefinic organotin compounds is an important factor with regard to the transmetalation reaction, since 3-butenyl- and 4-pentenyltin compounds were found not to react with *n*-butyllithium in ether. The action of phenyllithium on triphenylvinyllead gave vinyllithium and tetraphenyllead; on the other hand, phenyllithium added across the C=C bond of triphenylvinylgermane.

In previous papers of this series practical laboratory directions were given for the preparation of vinyllithium allyllithium and methallyllithium by the exchange reactions occurring between vinyl-, allyl- and methallyltin compounds and phenyl- and *n*-butyllithium

$$R_4Sn + 4\ C_6H_5Li \longrightarrow (C_6H_5)_4Sn + 4\ RLi\ (R = CH_2{=}CH- \text{ and } CH_2{=}CHCH_2-)$$

Transmetalations of this type are of value, since they make available organolithium reagents, the preparation of which either is difficult or impossible by the more conventional procedures. In order to make the most efficient use possible of the transmetalation reaction for this purpose, we have studied in greater detail the factors which affect this reaction. The results of some of our studies are discussed below.

Equilibria in Transmetalation Reactions.—It has been reported[2] that some transmetalation reactions represent equilibrium situations. This raised the question as to whether or not the exchange reaction between vinyltin and allyltin compounds and organolithium compounds might also involve an equilibrium reaction. As was shown in Part I,[3] the reaction

$$(CH_2{=}CH)_4Sn + 4\ C_6H_5Li \longrightarrow (C_6H_5)_4Sn + 4\ CH_2{=}CHLi$$

went to completion for all practical purposes, tetraphenyltin being formed in virtually quantitative yield. The insolubility of tetraphenyltin in ether[4] might possibly have been the factor which made this reaction proceed to near completion, and the possibility existed that in a system where both products were soluble the equilibrium (if one existed) might be such as to make the transmetalation of no preparative value. For this reason the solubility factor was examined. In the systems

$$n\text{-}Bu_3SnCH{=}CH_2 + C_6H_5Li \xrightarrow{Et_2O} n\text{-}Bu_3SnC_6H_5 + CH_2{=}CHLi \quad (a)$$

$$n\text{-}Bu_3SnCH{=}CH_2 + n\text{-}BuLi \xrightarrow{Et_2O} n\text{-}Bu_4Sn + CH_2{=}CHLi \quad (b)$$

all components are soluble in the ether medium. Tri-*n*-butylvinyltin and phenyllithium were allowed to react in ether solution during 2 hr.; the mixture then was treated with acetone and hydrolyzed. The products isolated included dimethylvinylcarbinol (63%), tri-*n*-butylphenyltin (73%) and tri-*n*-butylvinyltin (12%). Similarly, reaction b, in which the vinyllithium produced was characterized by its reaction with triethylbromosilane, gave tetra-*n*-butyltin in 87% yield, as well as triethylvinylsilane in 65% yield. Similar observations were made when the reaction of allyltri-*n*-butyltin with phenyllithium was studied; tri-*n*-butylphenyltin was isolated in 78% yield. Obviously the insolubility of tetraphenyltin is not the most important factor, since good conversions are obtained even when the organotin products are soluble in the reaction medium. The presence of the starting material, tri-*n*-butylvinyltin, has been noted among the products of the reaction between phenyllithium and tri-*n*-butylvinyltin. In order to ascertain whether this represents an equilibrium situation, the reverse reaction, that between vinyllithium and tri-*n*-butylphenyltin, was examined. In addition to tri-*n*-butylphenyltin (75%), a liquid representing *ca.* 5% yield of crude tri-*n*-butylvinyltin was obtained. This material was purified and identified positively as tri-*n*-butylvinyltin. To substantiate further this evidence, the forward reaction was carried out again, using the same reaction conditions. In this case tri-*n*-butylphenyltin and tri-*n*-butylvinyltin were isolated in yields of 76% and 10%, respectively.

An indirect, though substantial, piece of evidence in favor of an equilibrium situation was observed

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[1] Part III, D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).

[2] R. G. Jones and H. Gilman, *Chem. Revs.*, **54**, 863 (1954).

[3] D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

[4] W. Strohmeier and K. Miltenberger, *Chem. Ber.*, **91**, 1357 (1958).