[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

New Approaches to the Phosphinoborine Polymers[1]

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The trimer $(Me_2PBH_2)_3$ was made in 52% yield by the reaction of Me_2POCl with $NaBH_4$ in diglyme. The reaction of Et_2PCl with $NaBH_4$ in diglyme gave an air-stable oil appearing to be $(Et_2PBH_2)_3$; admixed $EtPCl_2$ led to similar material presumed to contain P–H bonds. Thermal decomposition of such material yielded H_2, the ethylphosphines, $(Et_2PBH_2)_3$ and boron-rich residues. The adduct $Me_2NPMe_2 \cdot BH_3$ (m.p. 12°; b.p. est. 211°) decomposed above 160° to give H_2, aminoborines, Me_2PH, $(Me_2PBH_2)_n$ (23%, mostly trimer), the rare biphosphine $P_2(CH_3)_4$ (20%) and non-volatile $[B_3H_5(Me_2P)_2Me_2N]_x$, having soft-plastic character. The solid adduct $Me_2NPMe_2(BH_3)_2$ above 200° gave H_2, Me_2PH, aminoborines $(Me_2PBH_2)_3$ (over 50% yield) and thermoplastic material wherein B atoms outnumbered the basic units at least two to one. The plasticity and high thermal stability of such materials can be explained in terms of a boron-hydride network structure which is rendered opener but less labile by entrapped basic units.

The further pursuit of the chemistry of phosphinoborine polymers seemed to require alternate methods of synthesis, for the original method employed the extremely malodorous and none-too available secondary phosphines.[2] We now have made compounds of the type $(R_2PBH_2)_3$ by three new methods not dependent upon dialkylphosphines. The first used sodium borohydride with dimethylphosphinyl chloride in the solvent "diglyme" (β,β'-dimethoxydiethyl ether) at temperatures up to 175°, with 52% conversion of the $(CH_3)_2POCl$ to $[(CH_3)_2PBH_2]_3$. The second method used diethylchlorophosphine with sodium borohydride in diglyme and gave a 70% yield of $[(C_2H_5)_2PBH_2]_3$.[3] The third method used the recently-discovered aminophosphine $(CH_3)_2NP(CH_3)_2$,[4] the BH_3-complexes of which can be heated to give good yields of $[(CH_3)_2PBH_2]_3$. The byproducts of this third method also were of interest: after the mono-BH_3 complex had been heated at 200°, it was possible to show that one of the volatile products was the scarcely-known compound $P_2(CH_3)_4$, the more direct synthesis and chemistry of which will be described in another paper.[5] An interesting higher phosphinoborine polymer also was observed. The heating of $(CH_3)_2NP(CH_3)_2(BH_3)_2$ produced another polymeric material having considerable thermal stability and leading to a purposive study of the formation of resins wherein boron-hydride polymer structures enclose amine or phosphine bases which render them thermoplastic and unexpectedly stable.[6] The first example of this principle was reported earlier.[7]

The Phosphinyl Chloride Method

Synthesis of Dimethylphosphinyl Compounds.—The compound $(CH_3)_2POCl$ (dimethylphosphinyl chloride) was made by the action of phosphorus pentachloride upon dimethylphosphinic acid. This acid was obtained by Grignard-methylation of R_2NPOCl_2 compounds and hydrolysis of the resulting dimethylphosphinic amides, all in accord with a general method described by Kosolapoff[8] except that here the intermediate compounds of the type R_2PONR_2 were isolated for the first time.

A 200 ml. diethyl ether solution of 81 g. of $(CH_3)_2NPOCl_2$ (0.5 mole, made by a partial aminolysis of $POCl_3$) was added during 90 min. to an 800 ml. ether solution of 1.1 mole of CH_3MgBr, first at −10° and later at the reflux temperature. A creamy-tan solid appeared and was kept mobile by the Hershberg stirrer. After 3.5 hr. of further refluxing, the condenser was replaced by a cold-finger at −78° and the product was released from its magnesium complex by addition of 77 g. of dry ammonia. After 4 hr. of stirring, the ether solution (with ether-washings from the white crystalline solid) was removed and evaporated, leaving 28 g. of a colorless oily liquid boiling at 89–91° (2 mm.). This substance, $(CH_3)_2PON(CH_3)_2$, had mol. wt. 121 in melting benzene (calcd., 121.1) and analysis 38.97% C, 10.08% H and 10.04% N (calcd., 39.67, 10.00 and 11.56). The density of the liquid at 20° was measured as 1.017 g./ml. Refractive index: $n_D = 1.453$ at 22.5°; yield, 46%.

The corresponding diethylamide $(CH_3)_2PON(C_2H_5)_2$ was made in a similar manner, in 35% yield. It was a liquid boiling at 131–42°/(26 mm.) or 78°/(1.5 mm.) and freezing to colorless needles just below room temperature. Refractive index: $n_D = 1.452$ at 23°. *Anal.* 44.7% C, 10.80% H and 8.00% N (calcd., 48.4, 10.81, and 9.38). The low results for C and N in both compounds are ascribed to their extremely hygroscopic character.

These dimethylphosphinic amides were converted to $(CH_3)_2POOH$ by 8-hr. refluxing with concentrated hydrochloric acid, which finally was evaporated off. The product was made basic by sodium hydroxide solution and the amine was removed by steam distillation; then the solution was acidified by HCl, evaporated and separated from sodium chloride by means of ethanol. The final crystallization was from benzene, out of which the ethanol and water had been boiled away. The yields of $(CH_3)_2POOH$ approached 75%; m.p. 91°,[2] unchanged by mixing with an authentic sample.

Treatment of 7.5 g. (80 mmoles) of $(CH_3)_2POOH$ with 16.7 g. (80 mmoles) of PCl_5 in benzene, with evaporation of the resulting HCl at 100°, produced 7.3 g. (80% yield) of $(CH_3)_2POCl$. This was purified by vacuum sublimation, m.p. 67°.

The Borohydride–Phosphinyl–Chloride Reaction.—A 40 ml. solution of 3.0 g. of $NaBH_4$ (80 mmoles, previously recrystallized from diglyme) was treated very slowly with 7.3 g. (65 mmoles) of $(CH_3)_2POCl$ dissolved in 40 ml. of diglyme, under dry nitrogen in a flask fitted with a −78° cold-finger. The highly exothermic reaction immediately precipitated sodium chloride and there was considerable evolution of hydrogen. The completeness of the initial reaction was tested by adding a further 100 mg. of $NaBH_4$; then the flask was heated slowly to 170° and held there until the evolution of hydrogen had virtually ceased (7.5 hr.). The precipitate was collected and weighed as 5.0 g., presumably including

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[2] A. B. Burg and R. I. Wagner, THIS JOURNAL, **75**, 3872 (1953).

[3] Our use of this method followed a private communication from Dr. Charles P. Haber (at the National Bureau of Standards in the year 1952), describing a reaction between $LiBH_4$ and $(C_6H_5)_2PCl$ in ether, leading to $[(C_6H_5)_2PBH_2]_3$.

[4] A. B. Burg and P. J. Slota, Jr., THIS JOURNAL, **80**, 1107 (1958).

[5] Initially presented in Technical Report WADC TR 56-82 (Part III) to Materials Laboratory, Wright Air Development Center, January, 1958.

[6] The formation of such resins from B_5H_9 will be the subject of another paper.

[7] A. B. Burg, THIS JOURNAL, **79**, 2129 (1957).

[8] G. M. Kosolapoff, *ibid.*, **71**, 369 (1949).

oxidized boron and possibly coprecipitated $NaBH_4$ (calcd. yield of NaCl, 3.8 g.). This solid gave a negative test for phosphorus. A droplet of liquid hanging from the cold-finger had a very strong dimethylphosphine odor but the question whether $(CH_3)_2PH\cdot BH_3$ had been formed (as the intermediate in the formation of the phosphinoborine) was not decided.

The clear solution was high-vacuum distilled, removing the solvent and leaving a difficultly volatile liquid. In the vacuum system at 170–185°, this developed large bubbles and delivered a sublimate of $[(CH_3)_2PBH_2]_3$ (obsd. m.p. 85°). The final yield of this was 2.5 g., representing 52% of the original $(CH_3)_2P$ groups. The non-volatile residue was a colorless glass.

The Chlorophosphine Method

The process $R_2PCl + NaBH_4 \rightarrow NaCl + R_2PH\cdot BH_3$; $3R_2PH\cdot BH_3 \rightarrow 3H_2 + [(CH_3)_2PBH_2]_3$ was tried first with $(C_2H_5)_2PCl$ because at the time (year 1955) this chlorophosphine was far easier to make than $(CH_3)_2PCl$. Indeed, at that time our only success in making $(CH_3)_2PCl$ was represented by a 3% yield (having the right mol. wt. and Cl^- analysis and volatility agreeing with later authentic samples)[4] from a dry reaction between KBH_4 and $(CH_3)_2POCl$ in a sealed tube at 185–200°. The choice of the diethyl compound may have been fortunate, for a later attempt at the $NaBH_4$–$(CH_3)_2PCl$ reaction gave scarcely any phosphinoborine, probably on account of the instability of $(CH_3)_2PCl$ under the experimental conditions An advantage of $(C_2H_5)_2PCl$ was the presence of $C_2H_5PCl_2$ in one of the samples, permitting an experimental variation in the direction of high polymers.

Synthesis of Diethylchlorophosphine.—Phosphorus trichloride was ethylated by refluxing with tetraethyllead,[9,10] finally yielding pure $(C_2H_5)_2PCl$ (b.p. 130–132°) or by briefer heating, an apparently azeotropic mixture containing 33 mole % of $C_2H_5PCl_2$ was obtained (b.p. 123–125°; Cl^- analysis, 37.08%). Both $Pb(CH_3)_4$[11] and $Cd(CH_3)_2$ were tried with PCl_3 and with PBr_3 in attempts to make either $(CH_3)_2PCl$ or $(CH_3)_2PBr$ by the simple reflux method; but these products were either too unstable or too difficult to isolate from the methylphosphorus dihalides, or both.

Diethylchlorophosphine with Sodium Borohydride.—A solution of 39.5 g. (0.32 mole) of $(C_2H_5)_2PCl$ in 100 ml. of diglyme was added during 45 min. to a solution of 16 g. (0.42 mole) of $NaBH_4$ in 50 ml. of diglyme, under dry nitrogen. The containing flask was equipped with a water-cooled reflux condenser and an outlet through a U-tube at −196° to a displacement bottle for rough measurement of the evolution of hydrogen. As the reaction went forward the temperature rose and 2.25 liters of hydrogen (gas at standard conditions) came off in the range 60–100°. The precipitated NaCl was filtered off and the solvent was removed by a very slow high-vacuum distillation at room temperature. With it came a water-insoluble component presumed to be some of the expected $(C_2H_5)_2PH\cdot BH_3$, for it yielded one liter of hydrogen during a 12-hr. refluxing at 170°. The main product—a viscous liquid which seemed to be mostly $(C_2H_5)_2PH\cdot BH_3$—was heated gradually to 180°, bringing the total evolved hydrogen to 0.295 mole (calcd., 0.32).

The liquid $[(C_2H_5)_2PBH_2]_3$ was isolated by an extensive series of low-pressure distillations, with some decomposition effects attributable to impurities, and with observation of a 3.5 g. fraction boiling in the range 211–242° (1.5 mm.)—possibly containing the tetramer but not further investigated. The estimated yield of the trimer was 22.8 g., or 70%. The purest sample distilled in the range 133–134° at a manometer reading of 1.5 mm. The mol. wt. (cryoscopic in benzene) was 302 (calcd. for trimer, 305.8); $n_D = 1.521$ at 25°. The analysis was done by digestion with nitric, perchloric and sulfuric acids and sodium molybdate:[12] found, 30.6% P; calcd., 30.4. The compound was perfectly stable in the open air, remaining a colorless oil for months in an open beaker. However, it could not be distilled at atmospheric pressure (at 300°) because of decomposition—again possibly due to impurities.

Mixed Ethylchlorophosphines with Sodium Borohydride.—An experiment with the mixture containing 33 mole % of $C_2H_5PCl_2$ was directed toward the synthesis of P-ethylated phosphinoborine trimer having some P–H bonds. The plan to eliminate hydrogen by interaction of P–H with B–H bonds (to form chains of trimer rings) did not succeed, for the heated product rearranged extensively to yield nearly pure $[(C_2H_5)_2PBH_2]_3$, hydrogen, ethylphosphines and a boron-rich residue. This result correlates with a tendency of various phosphino-polyborane materials to condense to thermally stable boron-rich high polymers—an effect which is more clearly observed in experiments involving aminophosphines.

A 46 g. sample of the mixed ethylchlorophosphines was brought to reaction with 17 g. of $NaBH_4$ in diglyme, yielding 6.78 l. of H_2 (calcd., 8.13) after 8 hr. of refluxing at 170°. The diglyme was removed by high-vacuum distillation (33–37°) and the tacky white residue was separated from sodium chloride by benzene-extraction. After three high-vacuum distillations a middle fraction was taken in the range 158–162° (3 mm.): yield, 17 g., or 52%; n_D 1.521 at 25°. This product appeared as a colorless oil which remained mobile at −78° but became glassy at lower temperatures. Its weight was unchanged after some weeks in an open beaker. Its average mol. wt. (cryoscopic in benzene) was 297, suggesting a mixture of $[(C_2H_5)_2PBH_2]_3$ and $(C_2H_5)_5HP_3B_3H_6$, but tetra-ethylated trimer-ring material also could have been present. An attempt at C–H analysis by molten potassium dichromate gave results lower than expected and there was no qualitative test for phosphate after the oil had been digested in a refluxing mixture of nitric and sulfuric acids.

An 8.5 g. sample of this oil was refluxed under dry nitrogen by means of a molten-metal bath at 330–385°, with displacement of gas equivalent to 65 mmoles of H_2. The other volatile products were 1.34 mmoles of C_2H_6, 2.18 mmoles of $C_2H_5PH_2$ and 9.63 mmoles of $(C_2H_5)_2PH$, all identified by their mol. wts. and vapor tensions. The remaining oil (5.5 g.) was distilled away from a boron-rich brown residue and repeatedly distilled under high vacuum for the selection of a 3 g. fraction approaching $[(C_2H_5)_2PBH_2]_3$ (m.p. −7 to −6°; obsd. b.p. 340°; mol. wt. in benzene, 300; 29.6% P). This also proved to be unstable under reflux at atmospheric pressure, again producing hydrogen, ethylphosphines and a brown residue; however, the extent of decomposition was less than for the original oil, suggesting that pure $[(C_2H_5)_2PBH_2]_3$ might have been entirely stable under atmospheric-pressure distillation.

The Aminophosphine Method

The chemically versatile aminophosphine $(CH_3)_2NP(CH_3)_2$[4] reacts with diborane, firmly bonding either one or two BH_3 groups; and both complexes give useful yields of $[(CH_3)_2PBH_2]_3$ upon heating in a closed system. However, some of the by-products are more interesting. One of these is dimethylphosphine, suggesting a method of making unusual secondary phosphines from the corresponding aminophosphines.[13] The formation of some $P_2(CH_3)_4$ from the mono-BH_3 complex probably occurs through dissociation to restore some aminophosphine for reaction with the dimethylphosphine.[5] The mono-BH_3 complex also forms a

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[9] M. S. Kharasch, E. V. Jensen and S. Weinhouse, *J. Org. Chem.*, **14**, 430 (1949).

[10] M. H. Beeby and F. G. Mann, *J. Chem. Soc.*, 413 (1951).

[11] We are happy to acknowledge the courtesy of the Ethyl Corporation in giving us samples of tetraethyllead and of tetramethyllead for this work.

[12] W. R. Simmons and J. H. Robertson, *Anal. Chem.*, **22**, 294 and 1177 (1950).

[13] A. B. Burg, THIS JOURNAL, **81**, 2148 (1959).

phosphinoborine polymer which may well have open-chain character, while the double-BH_3 complex leads to a glassy high-polymeric material especially rich in boron and having high thermal stability.

The Monoborine Adduct.—A 1.5816 g. sample (15.05 mmoles) of $(CH_3)_2NP(CH_3)_2$ was condensed at −196° upon a cold-finger within a vertical reaction-tube leading through a stop-cock to the high-vacuum apparatus. A 7.72 mmole sample of B_2H_6 was introduced and the reaction was allowed to occur as the cold-finger and main reaction-tube warmed from −78 to 0° during 18 hr. The product now appeared as a slightly volatile liquid at the bottom of the tube. Fractional condensation past the cold-finger at −78° let through 0.038 mmole of B_2H_6, while most of the complex collected as a solid (melting 9.5–12°) on the cold-finger; final composition: 1.021 BH_3 per $(CH_3)_2NP(CH_3)_2$. Much of this product was conveyed to an immersible tensimeter[14] by a 2-day high-vacuum distillation, and a substantial top fraction was distilled back. The remaining middle fraction gave the vapor-tension results shown in Table I.

TABLE I

VAPOR TENSIONS OF $(CH_3)_2NP(CH_3)_2\cdot BH_3$

t (°C.)	27.7	41.3	70.1	80.2	89.0	97.0
Pmm. (obsd.)	0.44	1.08	5.6	9.50	14.40	20.8
Pmm. (calcd.)	0.43	1.08	5.7	9.55	14.39	20.8

These can be extrapolated by the equation $\log P\text{mm.} = 6.5482 - 0.00464T + 1.75 \log T - 2964/T$ (derived by assuming that the Trouton constant is 21.00 cal./deg. mole), to give the normal b.p. as 211°, a temperature at which the rate of decomposition is considerable.

Thermal Decomposition of the Monoborine Adduct.—One sample of the complex $(CH_3)_2NP(CH_3)_2\cdot BH_3$ seemed unaffected by a 5-hr. heating at 130°, while another was extensively decomposed during 45 hr. at 160°. After 30 hr. in a sealed tube at 200°, a 4.67 mmole sample had produced 2.57 mmoles of H_2, 1.77 mmoles of $(CH_3)_2PH$, 1.78 mmoles of $[(CH_3)_2N]_2BH$ and 97.8 mg. of a mixture which could not be resolved by distillation. This could be shown by chemical means (as described below) to be composed of 0.743 mmole (42.3 mg.) of $(CH_3)_2NBH_2$ and 0.455 mmole (55.5 mg.) of the virtually unknown biphosphine $P_2(CH_3)_4$. Finally, high-vacuum sublimation brought out the $(CH_3)_2PBH_2$ units as trimer with some tetramer, amounting to 80.0 mg., a 23% yield. The white solid residue (mobile liquid at 200°) thus was calculated to have the approximate empirical formula $[B_3H_5(Me_2P)_2Me_2N]_x$. Its plastic character would suggest a relatively simple polymeric condition, probably with no very high mol. wt.

The 97.8 mg. fraction was treated with diborane, of which 0.522 mmole was absorbed, forming a non-volatile white solid and permitting the isolation of 0.123 mmole of $(CH_3)_2NB_2H_5$ and 0.620 mmole of $(CH_3)_2NBH_2$. Hence it could be inferred that the mixture had contained 42.3 mg. (0.743 mmole) of $(CH_3)_2NBH_2$. Conversion of 0.123 mmole of this to $(CH_3)_2NB_2H_5$ would require 0.062 mmole of B_2H_6, so that the remaining 55.5 mg. of the 97.8 mg. fraction must have absorbed 0.460 mmole of B_2H_6. Taken as $P_2(CH_3)_4$, this 55.5 mg. would correspond to 0.455 mmole, in agreement with the assumption that the non-volatile solid was $P_2(CH_3)_4(BH_3)_2$. This material, although non-volatile at room temperature, could be sublimed very slowly but completely at 100°, in accord with the observed volatility of an authentic sample of the double-BH_3 adduct of $P_2(CH_3)_4$.[5]

Another experiment, wherein the 15.05 mmole sample of $(CH_3)_2NP(CH_3)_2\cdot BH_3$ was heated for 115 hr. at 210°, gave essentially the same results, including a fraction containing $(CH_3)_2NBH_2$ and $P_2(CH_3)_4$. A portion of this was treated with diborane, to form a non-volatile solid weighing 43.3 mg. This was analyzed for phosphorus by the Simmons–Robertson method:[12] found, 18.7 mg. P; calcd. for $P_2(CH_3)_4(BH_3)_2$, 18.3 mg.

The Double-Borine Adduct.—Table II summarizes the numerical data of three experiments on the formation and thermal decomposition of $(CH_3)_2NP(CH_3)_2(BH_3)_2$. The exploratory expt. 1 began with a 23% excess of diborane, the action of which was indicated by fog-formation as the aminophosphine melted (−97°); however only 0.72 B_2H_6 was absorbed per $(CH_3)_2NP(CH_3)_2$ at first. The approach to a 1:1 ratio required 14 hr. at 22°. At all stages of formation the adduct was a solid. After the initial heating, 0.03 mmole of $(CH_3)_2NH$ was removed but a trace of $(CH_3)_2PH\cdot BH_3$ was put back for further heating with the contents of the resealed tube. After the 130° heating all volatile products were removed and the white non-volatile residue was heated in the open air, with no very obvious effect except a flash of white light, above 300°.

TABLE II

THERMAL DECOMPOSITION OF $(CH_3)_2NP(CH_3)_2(BH_3)_2$

Expt. no.	Reactants (mmoles)		Time (days)	Temp. (°C.)	Products (total mmoles)[d]				
	Me_2NPMe_2	B_2H_6			H_2	Me_2PH	Me_2NBH_2	$(Me_2N)_2BH$	$(Me_2PBH_2)_3$
1	0.93	0.88	1.8	92	0.28	..	..	..	....
			23.0	130	0.95	0.25	..	0.28	(Obsd.)
2	18.74	18.47	2.6	170	28.7	3.00	2.59	6.94	nm
	(Residue only)		14.1	220	28.9	3.40	2.59	7.03	2.48
	(Residue only)		0.02	320	30.76	3.90	2.60	7.48	2.48
3	21.18	20.73	0.04	220	14.19	nm	nm	nm	nm
		+3.35	0.02	220	14.54	1.80[a]	(Obsd.)[a]	1.1[a]	nm
			1.0	250	23.78	..	Nil	5.85	nm
			2.5	280	30.22	0.19	0.74[b]	7.42[c]	3.637

[a] Product returned to the bomb-tube for further reaction. [b] Also 0.44 mmole of Me_2NH obtained from sublimation of the benzene extract. [c] Also 0.30 mmole of $(Me_2N)_3B$. [d] nm means probably present but not isolated for measurement.

In expt. 2 the diborane was allowed to flow slowly toward the aminophosphine in the bottom of a sealable tube, where it was absorbed with noticeable evolution of heat. Finally, the resulting white solid was heated to 100° with excess diborane, bringing its composition to 0.986 B_2H_6 per $(CH_3)_2NP(CH_3)_2$. The adduct, which was not observably volatile at room temperature, was twice heated in the sealed and resealed tube, with removal of the listed volatile products after each heating. After the 220° heating, the empirical formula of the non-volatile product was $[B_{16}H_{15}(Me_2P)_6Me_2N]_x$. The 320° heating under vacuum brought this to $[B_{16}H_{12}(Me_2P)_6Me_2N]_x$, corresponding to 31.2% P. The material was mostly a brownish glass, with minor proportions of oil and gum. After benzene-extraction, the nearly white insoluble glass was analyzed for phosphorus by the Simmons–Robertson[12] method, showing 28.0% P. The yield of $[(CH_3)_2PBH_2]_3$ from this experiment was 40.0%.

Expt. 3 began with the absorption of B_2H_6 by $(CH_3)_2NP(CH_3)_2$ at −78° followed by a 30-min. heating at 90° to complete the formation of the double-BH_3 adduct. After the 50-min. heating at 220°, the H_2 was pumped off and a 15% excess of B_2H_6 was added for reaction with the volatile bases. Then the two further successive heatings were done in a sealed tube with little removal of volatiles (except H_2) between heatings. The final yield of $[(CH_3)_2PBH_2]_3$ (m.p. 86°) represented 51.5% of the aminophosphine. The empirical formula of the non-volatile white thermoplastic glass was computed to be $[B_{20}H_{37}(Me_2P)_7(Me_2N)_3]_x$. The high proportion of B-connected hydrogen (relative to that in the glass from expt. 2) is attributed to the excess diborane, which used up most of the expected $(CH_3)_2PH$, presumably forming many $(CH_3)_2PBH_2$ units which were trapped in the polymer instead of being delivered as trimer.

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[14] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, 59, 785 (1937).

The general structural principle of such polymers probably relates closely to that of the thermoplastic materials derived from trimethylamine and pentaborane-9.[7] It is not difficult to imagine a boron-hydride polymer network of a type suggested by the structure of decaborane[15] or the more condensed metal polyborides.[16] Now if basic units were inserted into such a network, the greater availability of bonding electrons would lead to a decrease in the amount of low-order boron–boron bonding. Hence there would be less cross-linking and thermoplasticity would become possible. This idea offers ample opportunity for trapping of phosphinoborine units, rings or chains (as well as tertiary amines or phosphines or aminopolyborane structures) in highly polymeric aggregates. The recently-determined structural pattern of $(CH_3CN)_2B_{10}H_{12}$[17] shows a relatively simple example of the kind of base-to-B-network bonding here considered.

An expected effect of the entrapped base units would be to bring the average bonding of the boron atoms closer to the four-coördinate situation. Thus the lability of bonding would be decreased and there would be less opportunity for H atoms to congregate near certain boron atoms as a first step toward easily activated processes forming H_2. Hence it is not wholly surprising that these base-inclusive polymers show much higher thermal stability than the $(BH)_x$ type of polymer.

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[15] J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

[16] Reviewed by R. Kiessling, *Acta Chem. Scand.*, **4**, 209 (1950).

[17] J. v.d.M. Reddy and W. N. Lipscomb, THIS JOURNAL, **81**, 754 (1959).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Chemistry of the C_4H_8P Ring: the Aminophosphine $(CH_3)_2NPC_4H_8$, the Cyclophosphine C_4H_8PH and the Tetracyclic Trimer $(C_4H_8PBH_2)_3$[1]

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The new amino-cyclophosphine $(CH_3)_2NPC_4H_8$ (liquid, b.p. est. 170°) was made from $(CH_3)_2NPCl_2$ and $BrMgC_4H_8MgBr$. It forms a 1:1 adduct with CH_3I and reacts with 2HCl to make C_4H_8PCl (liquid, b.p. est. 165°), reconvertible to $(CH_3)_2NPC_4H_8$ by reaction with $2(CH_3)_2NH$. The slightly volatile liquid adduct $(CH_3)_2NPC_4H_8 \cdot BH_3$ on heating forms the new cyclic C_4H_8PH (30% yield; m.p. −88°; b.p. est. 105°), aminoborines and a trace of the tetracylic trimer $(C_4H_8PBH_2)_3$ (m.p. $169.3 \pm 0.4°$). This trimer was made almost quantitatively from the liquid complex $C_4H_8PH \cdot BH_3$. The ring structure of C_4H_8PH was confirmed by its infrared spectrum. For the isolation of C_4H_8PH, the accompanying compound $[(CH_3)_2N]_2BH$ was converted by 2HCl to $(CH_3)_2NH_2Cl$ and $[(CH_3)_2NBHCl]_x$.

Cyclic phosphines of the type $C_nH_{2n}PH$ seem not to have been reported, although numerous efforts have been made toward their synthesis. We now have made such a phosphine, through a double-Grignard synthesis of the aminophosphine $(CH_3)_2NPC_4H_8$. Just as the prototype aminophosphine $(CH_3)_2NP(CH_3)_2$[2] forms the slightly volatile liquid adduct $(CH_3)_2NP(CH_3)_2 \cdot BH_3$,[3] so also the new $(CH_3)_2NPC_4H_8$ reacts with a deficient proportion of diborane to form the still less volatile liquid $(CH_3)_2NPC_4H_8 \cdot BH_3$. On heating, this adduct produces hydrogen, dimethylamine, the aminoborines, the expected phosphinoborine polymers (including resinous material) and the corresponding phosphine, C_4H_8PH.

The phosphinoborine trimer $(C_4H_8PBH_2)_3$, which is a minor product of this decomposition, can be made almost quantitatively from the adduct $C_4H_8PH \cdot BH_3$, just as $[(CH_3)_2PBH_2]_3$ can be made from $(CH_3)_2PH \cdot BH_3$.[4] Assuming the same kind of $(PB)_3$ ring as in $[(CH_3)_2PBH_2]_3$,[5] this new phosphinoborine trimer would have an unusual paddle-wheel structure, with the three C_4H_8P rings in planes perpendicular to the B–P–B planes of a somewhat puckered $(PB)_3$ ring.

Part of the evidence proving the formula of $(CH_3)_2NPC_4H_8$ was its conversion by HCl to the corresponding chlorophosphine C_4H_8PCl, and the reversion of this to the aminophosphine by the action of dimethylamine. Final evidence of the C_4H_8P ring came from the infrared spectrum of C_4H_8PH, which has significant features in common with the spectra of C_4H_8NH and C_4H_8O.

The Amino-cyclophosphine

Synthesis.—Two solutions, one containing the double Grignard reagent $BrMgC_4H_8MgBr$ made from 200 g. (920 mmoles) of 1,4-dibromobutane in 600 ml. of diethyl ether and the other containing 136 g. (930 mmoles) of $(CH_3)_2NPCl_2$ in 500 ml. of ether, were added simultaneously to 500 ml. of ether at −78°. This process was carried out during 2 hr., in a 2-l. three-neck flask with a Hershberg stirrer and a slow stream of dry nitrogen. The $(CH_3)_2NPCl_2$ was kept slightly in excess throughout the process. Crystallization of the double Grignard reagent in the dropping funnel was minimized by the use of an infrared lamp. The first observable reaction was the precipitation of hard white crystals. After the mixing was complete, the flask was held at −78° for an hour and then warmed to room temperature during another hour. Near room temperature the crystals changed to a light-brown gum which made stirring difficult. After 1 hr. of refluxing, the solution was decanted off and the amino-cyclophosphine was isolated by column-distillation. The final purification was done by micro-column distillation (0° reflux) under high vacuum. The main yield was 9 g.

The recovered ether was returned to the flask containing the gummy residue and the stirred mixture was treated with

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