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Liquid Ammonia Chemistry of the Methyl Phosphines

BY ROSS I. WAGNER[1] AND ANTON B. BURG

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Good yields of CH_3PH_2 and $(CH_3)_2PH$ are obtained by liquid ammonia reactions of the type $2e^- + 2PH_3 \rightarrow 2PH_2^- + H_2$; $CH_3Cl + PH_2^- \rightarrow Cl^- + CH_3PH_2$. The conversion of CH_3PH_2 to $(CH_3)_2PH$ by this method is not always efficient, for CH_3PH_2 is a weaker protic acid than PH_3, and may have some hydridic tendency. A definite hydridic reaction is shown by $(CH_3)_2PH$ in the presence of amide ion, with which it forms an orange-colored complex, and then ammonolyzes to a salt from which the bis-phosphinoamine $(CH_3)_2P(NH)P(CH_3)_2$ (m.p. 39.5°, v.t. 3.2 mm. at 27°) is obtained by action of NH_4Br. This amine has a small tendency to disproportionate, yielding ammonia and other products, and may have been formed through disproportionation of $(CH_3)_2PNH_2$. The orange complex is easily decomposed into $(CH_3)_2PH$ and amide, or on treatment with CH_3Cl gives a 92% yield of $(CH_3)_3P$.

In relation to studies of the phosphinoborine polymers[2] it was necessary to develop new methods of synthesis of methyl and dimethyl phosphines, since the earlier bomb tube methods[3,4] gave only very small yields relative to the required effort. Of a number of approaches which were tried, the best was based upon the use of metals in liquid ammonia, according to the equations (1) $2PH_3 + 2e^- \rightarrow 2PH_2^- + H_2$; (2) $CH_3Cl + PH_2^- \rightarrow CH_3PH_2 + Cl^-$; (3) $2CH_3PH_2 + 2e^- \rightarrow 2CH_3PH^- + H_2$; (4) $CH_3Cl + CH_3PH^- \rightarrow (CH_3)_2PH + Cl^-$. Step (1) has long been known[5] and the others were planned by extrapolation from similar studies of arsine.[6] Either sodium or calcium was employed as the source of electrons for steps (1) and (3), and the corresponding chlorides were precipitated in steps (2) and (4). The yields of CH_3PH_2 by this method were not far from quantitative, with 87% recovery; for $(CH_3)_2PH$ the best was 67%, based upon CH_3PH_2.

The observations of H. C. Brown, *et al.*, on the sharp increase of electron-donor bonding power of methylphosphines with increasing methylation,[7] led to the expectation that the removal of a proton from a phosphine would become more difficult in the same order. In fact, reaction (1) is fast, but (3) is definitely slower and harder to complete without side-reactions leading to an impairment of the yield of dimethylphosphine. Furthermore, all attempts to form an authentic salt of the $(CH_3)_2P^-$ ion from sodium and $(CH_3)_2PH$ failed on account of an ammonolysis reaction in which the P–H bond acted not as a proton source, but as a hydride, much as the Si–H bond does in the reaction of $(C_2H_5)_3SiH$ with amide in liquid ammonia.[8]

The hydridic reaction of dimethylphosphine with sodium in liquid ammonia occurred in such a manner as to suggest that the first step was an accelerated amide formation, and the next an amide-promoted ammonolysis of the P–H bond. Some light was thrown on the latter aspect by the observation that sodium amide and dimethylphosphine (each virtually insoluble in liquid ammonia) together dissolve in liquid ammonia at −78° to form a deep-orange-colored solution, which then slowly gives off one H_2 at higher temperatures, without reprecipitation of sodium amide. The resulting sodium salt evidently is some kind of phosphinamide—either $Na(CH_3)_2PNH \cdot xNH_3$ or $Na(CH_3)_2PNP(CH_3)_2 \cdot xNH_3$—for its treatment with ammonium bromide leads through a product of uncertain

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

(3) A. W. Hofmann, *Ber.*, **4**, 605 (1871).

(4) N. R. Davidson and H. C. Brown, THIS JOURNAL, **64**, 718 (1942).

(5) A. Joannis, *Compt. rend.*, **119**, 557 (1894).

(6) W. C. Johnson and A. Pechukas, THIS JOURNAL, **59**, 2068 (1937); also, private communications from W. C. Johnson are gratefully acknowledged.

(7) H. C. Brown, E. A. Fletcher, E. Lawton and S. Sujishi, Abstracts of Papers Presented at the 121st National Meeting of the American Chemical Society, p. 9N (1951).

(8) C. A. Kraus and W. K. Nelson, THIS JOURNAL, **56**, 195 (1934).

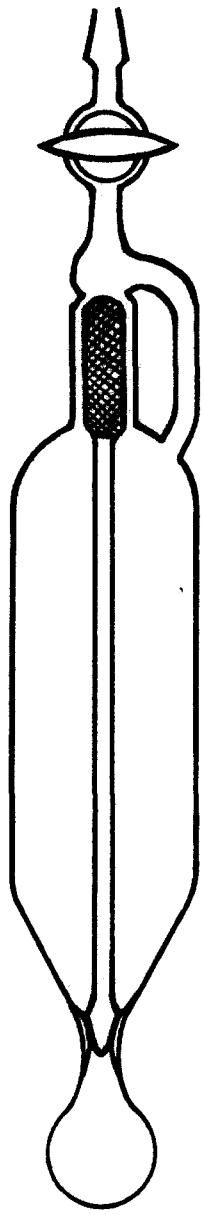

Fig. 1.—Magnetic separatory funnel.

constitution to a volatile bisphosphinoamine, $(CH_3)_2P(NH)P(CH_3)_2$, which undergoes a partial disproportionation at moderately elevated temperatures.

The constitution of the original deep-orange solute is difficult to judge. Since both components, $NaNH_2$ and $(CH_3)_2PH$, are only very slightly soluble in ammonia, it is suggested that amide attaches to phosphorus, forming a complex ion in which the electron-octet of P is exceeded; then the high electron-density on P would promote the hydridic behavior of the P–H bond. Such a complex ion would not be expected to be very stable, and in fact the formation of the orange solution is very definitely reversible even at −78°.

The orange solution reacts with CH_3Cl to give a very high yield of $(CH_3)_3P$, and one might explain this result either as an addition of CH_3^+ groups to the hypothetical $(CH_3)_2P^-$ ion or as a similar reaction with the amide-complex ion of $(CH_3)_2PH$, with a loss of H^+ and NH_2^- from the resulting aggregate, to form ammonia. The $(CH_3)_2P^-$ hypothesis lacks verisimilitude because all attempts to isolate a pure salt of that anion, by several different approaches, have failed; but an ammoniate of it still could be present as a minor component of an elaborate equilibrium system. On the other hand, the rapid addition of CH_3Cl to $(CH_3)_2PH$ (but not to NH_2^-) at −78° would require a fairly special mechanism. Possibly the attachment of NH_2^- to $(CH_3)_2PH$ strongly activates the unshared electrons of P for displacement of Cl^- from CH_3Cl. The state of this solution evidently deserves further study.

It is possible that CH_3PH_2 is involved with amide in a similar situation, less favorable to the hydridic reaction but tending to impair step (3) in the preparation of $(CH_3)_2PH$. If so, it might be possible to obtain nearly quantitative yields of $(CH_3)_2PH$ by adding CH_3PH_2 to $NaNH_2$ or KNH_2 in liquid ammonia at −78°, and treating the product with methyl chloride quickly, allowing little time for any hydridic reaction to occur.

Experimental Part

Preparation of Phosphine.—Pure phosphine was prepared by dropwise addition of aqueous potassium hydroxide to a resublimed sample of phosphonium iodide. For storage, it was condensed from the high vacuum apparatus into a steel cylinder.

Methylation of Phosphine.—In the first experiment, a solution of 3.65 g. of sodium in 250 ml. of liquid ammonia was treated with enough phosphine to discharge the blue color (in an apparatus adapted from the literature)[9] and the light-yellow solution was treated with the calculated proportion of CH_3Cl, discharging the yellow color and precipitating NaCl. The resulting two-phase liquid system was distilled off and treated with sodium, introduced in 50-mg. capsules. At −78° the first 100 mg. of sodium was used up in ten minutes, but three hours were required to fade the blue color of 100 mg. of sodium after 2.9 g. had been added, corresponding to conversion of 79% of the CH_3PH_2. The chrome-yellow solution now was treated with CH_3Cl in amount equivalent to the sodium used up at this point, and the denser of the two liquid phases, chiefly $(CH_3)_2PH$, was separated by means of the magnetically operated separatory funnel indicated in Fig. 1; this worked very well except that some of the oily $(CH_3)_2PH$ adhered to the walls above the cut-off. Since $(CH_3)_2PH$ has some small solubility in liquid ammonia, some but not all of the dissolved product was recovered by column-fractionation of the ammonia phase. The yield of $(CH_3)_2PH$ actually formed was estimated as 25–30%, based upon the original phosphine. Its purity was indicated by its vapor tension of 342 mm. at 0° (lit. 338).[4]

The next method began with the formation of $Ca(PH_2)_2 \cdot 6NH_3$ from Ca and PH_3 in liquid ammonia.[10] After removal of the solvent, the salt was decomposed *in vacuo* at 50° to form CaPH, PH_3 and NH_3, with 82% recovery of the indicated phosphine. Then the CaPH, which in the dry state would not react with CH_3Cl, was suspended in stirred liquid ammonia and converted by CH_3Cl to $CaCl_2 \cdot 8NH_3$ and $(CH_3)_2PH$; yield 33%. This method had two major disadvantages: the uncertainty of getting CaPH cleanly, without forming Ca_3P_2 or retaining $Ca(PH_2)_2$, and the tedious character of the heterogeneous final step.

Finally, the original process was tried again, using 40 g. of calcium (instead of sodium) in 2 liters of liquid ammonia. This time the CH_3PH_2 was isolated after step (2), in 87% yield, by means of a fractionating column having a special liquid-separatory reflux head (shown in Fig. 2), operating at −78°. Ordinary fractionation would not work well because the immiscible methylphosphine underwent ammonia vapor distillation and so preceded the bulk of the ammonia. Hence the head was arranged to collect a pool of CH_3PH_2 while returning the less dense liquid ammonia. At the end of the process the pool was drained by cooling the side-arm receiver; the relatively small amount of ammonia which followed it was removed by means of the magnetic separatory funnel. Another difference from the original process was in step (3): the calcium (37 g.) was first dissolved in the liquid ammonia (1.7 liters) and the CH_3PH_2 was distilled in as rapidly as feasible, at −78°. Then the methyl chloride was introduced rapidly (on a stream of dry nitrogen to avoid stoppage of the delivery tube) so that the dimethylphosphine was formed before any serious disturbance by side reactions could occur. The product was isolated by means of the separatory-head column and the magnetic funnel; the yield of $(CH_3)_2PH$ after purification was 72.5 g. (1.17 moles, or 67.2%, based upon CH_3PH_2).

The Reaction of $(CH_3)_2PH$ with Sodium in Liquid Ammonia.—In an attempt to form the salt $NaP(CH_3)_2$, 18.1 cc.[11] of $(CH_3)_2PH$ and 17.4 mg. (16.95 cc.) of Na, in 0.5 ml. of liquid ammonia, changed from blue to deep orange during 3.5 hours at −40 to −35°. The evolved hydrogen now was measured as 11.06 cc., or 130% of that expected from the equation $2Na + 2(CH_3)_2PH \rightarrow H_2 + 2NaP(CH_3)_2$. The volatile components were distilled out *in vacuo* and separated, with recovery of 6 cc. of $(CH_3)_2PH$. Hence the reaction had produced nearly one H_2 per $(CH_3)_2PH$ used up, or more if the recovery of $(CH_3)_2PH$ was incomplete. The purity of the hydrogen was demonstrated by combustion over CuO; hence the production of so much must be ascribed to a hydridic reaction. A similarly high yield of hydrogen was found in two other experiments at different concentrations of reactants.

The Reaction of $(CH_3)_2PH$ with $NaNH_2$.—Sodium amide was made from 25.2 mg. (24.5 cc.) of sodium by means of a trace of ferric nitrate in 0.5 ml. of liquid ammonia: H_2,

(9) C. A. Kraus and C. L. Brown, THIS JOURNAL, **52**, 4034 (1930).

(10) C. Legoux, *Compt. rend.*, **209**, 47 (1939).

(11) Throughout this paper, the term "cc." refers to the volume which the designated substance would occupy as a gas at standard conditions.

12.20 cc. (99.6%). Then 24.5 cc. of $(CH_3)_2PH$ was condensed upon the frozen $NaNH_2$–NH_3 system, and allowed to mix in at the melting point, forming a solution having the deep orange color noted before. At −30° this solution produced 1.0 cc. of H_2 in the first 15 minutes. Toward the end of the reaction, as the orange color was fading toward yellow, the temperature was raised to −10°, and after four days the total hydrogen amounted to 24.47 cc.—just one H_2 per $(CH_3)_2PH$ or $NaNH_2$. Two similar experiments on a far larger scale, and at temperatures up to 25°, gave the same conclusion: that $(CH_3)_2PH$ with an equivalent amount of $NaNH_2$ yields one H_2 per mole.

Formation of $(CH_3)_2P(NH)P(CH_3)_2$.—Sodium amide made from 472.1 mg. of Na (460 cc.) was treated with 405 cc. of $(CH_3)_2PH$ in 9 ml. of liquid ammonia, in a heavy-walled bomb tube. Effervescence was seen at room temperature, and during three days the deep orange color faded to yellow. The hydrogen now was pumped off and measured as 407.3 cc., or 1.005 H_2 per $(CH_3)_2PH$. The solution was treated with 1.8 g. of NH_4Br, which discharged the yellow color, with precipitation of NaBr. Then all material volatile at 65° was distilled off *in vacuo* and the ammonia fraction was removed through a reflux-head at −78°, leaving a volatile residue which melted on warming to room temperature. Repeated fractional condensation, using traps at 0, −78, and −196°, brought out more ammonia and finally yielded a volatile white solid which melted sharply at 39.5°. The vapor density of this product indicated the molecular weight to be 137.6; calcd. for $(CH_3)_2P(NH)P(CH_3)_2$, 137.1. Microanalysis: 35.15% C, 9.57% H and 11.06% N; calcd. 35.04, 9.56 and 10.22.

The vapor tensions of this solid bis-phosphinoamine: (3.21 mm. at 27.1°, 4.13 at 30.0°, 5.40 at 33.5°, and 7.22 at 37.0°) agreed well enough with the equation $\log_{10} p_{mm.} = 11.240 - 3221/T$ (calcd. values 3.27, 4.14, 5.47 and 7.18) to indicate a single substance, as suggested also by the sharpness of the melting point; however the vapor tension curve ($\log p$ *vs.* $1/T$) for the liquid showed such an extreme downward-concavity that a Nernst-approximation equation based upon points in the range 8–32 mm. went through a maximum of 54 mm. at 120°. Such behavior could be explained by a limited formation of a more volatile substance at medium temperatures—in amounts which became a less important fraction of the vapor at higher temperatures.

For a direct test of this effect, a 15.4-cc. sample of the compound was heated in a sealed tube for 15 hours at 145°, yielding 1.4 cc. of ammonia and a trace of liquid impurity which could not readily be separated from the main solid sample. A disproportionation clearly had occurred to a limited extent—presumably forming ammonia and a tris-phosphinoamine $[(CH_3)_2P]_3N$, but not necessarily limited to these substances. The question whether the original product of the NH_4Br treatment was a mono-phosphinoamine $(CH_3)_2PNH_2$, disproportionating easily to form the bis-phosphinoamine and ammonia, or only an ammoniated bis-phosphinoamine, was not decided.

Reversal of the $(CH_3)_2PH$-NH_2^- Addition Reaction.—Sodium amide was made from 176.5 mg. of Na (172.0 cc.) in 2 ml. of liquid ammonia; then the equivalent amount of $(CH_3)_2PH$ was added at −78° and the mixture was stirred magnetically for one hour to ensure completion of the addition reaction. Now the solvent ammonia was distilled off at −78°, leaving a more and more viscous residue, which finally was pumped at −78°, toward a trap at −196°, for some 30 hours. The H_2 now amounted to 0.75 cc. and the $(CH_3)_2PH$, 100.8 cc.—isolated from ammonia by addition of $B(CH_3)_3$ and repeated fractional condensation through a trap at −23°, which passed the $(CH_3)_2PH{\cdot}B(CH_3)_3$ but held back the $H_3N{\cdot}B(CH_3)_3$. A further 25.6 cc. of $(CH_3)_2PH$ was recovered by pumping the now solid residue for 30 minutes at −23°, and then 30 minutes at 25°; total $(CH_3)_2PH$ now 73.4% of the original; total H_2, 1.31 cc.

Conversion of $(CH_3)_2PH$ to $(CH_3)_3P$.—The solid which remained, after removal of 73.4% of the $(CH_3)_2PH$ from the amide-addition product in the preceding experiment, was redissolved in liquid ammonia and treated with 183.0 cc. of CH_3Cl at −78°. After six hours 0.56 cc. of H_2 and 25.0 cc. of $(CH_3)_3P$ were isolated; yield of the latter, 55%, based upon the unrecovered $(CH_3)_2PH$.

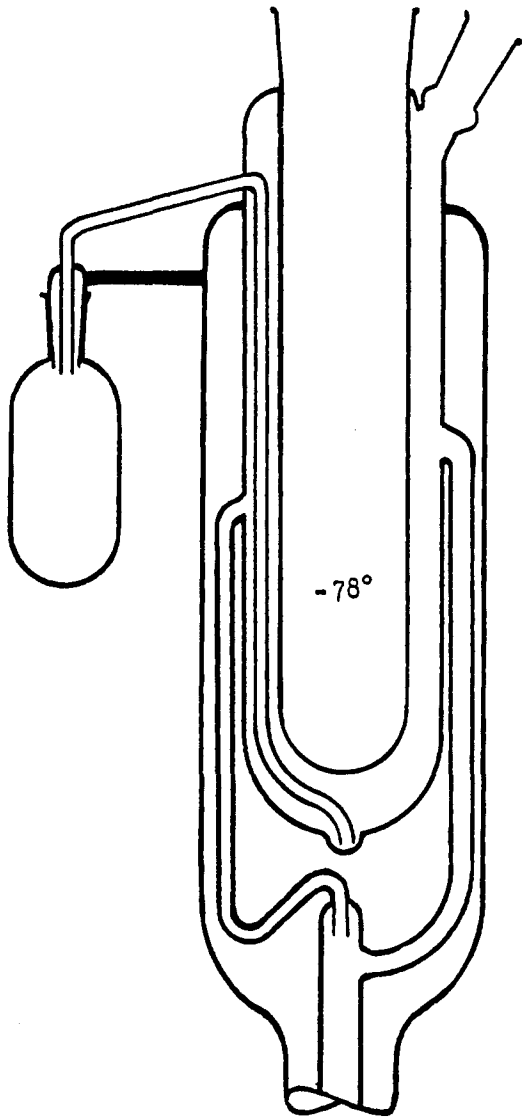

Fig. 2.—Liquid separatory reflux head.

For a nearly quantitative result, a solution of 75.5 cc. of $(CH_3)_2PH$ and 74.3 cc. of sodium amide in liquid ammonia was treated with 75.5 cc. of CH_3Cl, with 30 minutes of stirring at −78°. All material volatile at room temperature now was distilled off, with isolation of 0.30 cc. of H_2 and 68.1 cc. of $(CH_3)_3P$. The latter was characterized by its melting point (−88°, lit. −85°)[12] and vapor tension at 0° (162.0 mm., lit. 161.3).[13] The yield was nearly 92%, based upon the least component, the sodium amide.

LOS ANGELES 7, CALIFORNIA

(12) N. R. Davidson and H. C. Brown, THIS JOURNAL, **64**, 319 (1942).

(13) E. J. Rosenbaum and C. R. Sandberg, *ibid.*, **62**, 1622 (1940).