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

Dimethylaminodimethylphosphine[1]

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The new-type aminophosphine $(CH_3)_2NP(CH_3)_2$ (m.p. −97°, b.p. 99.4°) has been made by a Grignard action on $(CH_3)_2NPCl_2$. The N–P bond is susceptible to further Grignard action, offering a new way to make R_2PR'-type phosphines. The methyl iodide complexes $(CH_3)_2NP(CH_3)_3I$ and $(CH_3)_2NP(CH_3)_3HgI_3$ were made, and the attachment of CH_3 to P rather than to N is explained on an electronic basis. A fast HCl reaction converts $(CH_3)_2NP(CH_3)_2$ to $(CH_3)_2PCl$ (m.p. −1.4°, b.p. est. 73°), which reacts with $(CH_3)_2NH$ to restore $(CH_3)_2NP(CH_3)_2$. These reactions can be made nearly quantitative in spite of complications due to the formation of a very stable $(CH_3)_2NP(CH_3)_2$–$(CH_3)_2PCl$ adduct and an unstable $(CH_3)_2PCl$–HCl compound. Ammonia attacks $(CH_3)_2NP(CH_3)_2$ to form $(CH_3)_2NH$, $[(CH_3)_2P]_2NH$ and $[(CH_3)_2P]_3N$.

The wide chemical variety offered by the phosphinoborine polymers[2] makes it desirable to seek new approaches to their synthesis. One route is through the new formula-type R_2NPR_2, the simplest example of which, $(CH_3)_2NP(CH_3)_2$, we described at a recent National Meeting.[3] This represents a stabilized version of the $(CH_3)_2PNH_2$ which was postulated as an intermediate in the formation of $[(CH_3)_2P]_2NH$.[4] It also bears an analogy to the $(CF_3)_2PN(CH_3)_2$ which recently was made elsewhere.[5] This paper describes the synthesis and some of the chemical consequences of $(CH_3)_2NP(CH_3)_2$. Its use for making known and new types of phosphinoborines will be the subject of another publication.

Our method of making $(CH_3)_2NP(CH_3)_2$ was the action of CH_3MgBr upon $(CH_3)_2NPCl_2$, which had been made by a one-stage aminolysis of phosphorus trichloride. The immediate yields of the desired aminophosphine never exceeded 48%, because the Grignard reagent attacked the N–P bond almost as effectively as the P–Cl bond. Probably some $(CH_3)_2PCl$ was formed, for a considerable additional yield of $(CH_3)_2NP(CH_3)_2$ could be obtained by attacking some of the residues with dimethylamine. However, there may also have been some interference due to the formation of a very stable adduct between $(CH_3)_2NP(CH_3)_2$ and $(CH_3)_2PCl$.

The reaction of CH_3MgBr with $(CH_3)_2NP(CH_3)_2$ produced $P(CH_3)_3$ so easily as to suggest that the use of other Grignard reagents would offer an effective new way to make compounds of the rare type R_2PR'. However, the substitution of CH_3 for $(CH_3)_2N$ groups in $[(CH_3)_2N]_3P$ did not succeed, even in butyl ether at its boiling point. One reason might be the stability of the complex which the tris-amino-phosphine formed with the Grignard reagent.

In the course of this study there was occasion to make the methyl iodide adduct $(CH_3)_2NP(CH_3)_3^+I^-$ and its mercury complex-salt $(CH_3)_2NP(CH_3)_3HgI_3$. It was possible to show that the extra methyl group was attached to phosphorus rather than nitrogen, suggesting that the greater base strength, or electron-donor bonding power directed externally, resides with the phosphorus. This effect is intelligible, for the base strengths of $(CH_3)_2NH$ and $(CH_3)_2PH$ are not far different, but in $(CH_3)_2NP(CH_3)_2$ the donor-bonding power of N must be weakened by interaction of its lone electron-pair with an appropriately directed 3d orbital of P. The lone-pair on P cannot thus interact with N, and its base action would be enhanced by the inductive effect of N-electrons.

The aminophosphine $(CH_3)_2NP(CH_3)_2$ reacts very readily with hydrogen chloride to form the rare compound $(CH_3)_2PCl$, which easily converts back to the aminophosphine by reaction with dimethylamine. The aminophosphine also reacts very easily with ammonia to form poly-phosphino-amines, with liberation of dimethylamine. This reaction offers a new approach to the bis- and tris-phosphino-amines, such as were encountered in the earlier study of the liquid ammonia chemistry of the methylphosphines.[4] The thermal decomposition of these phosphino-amines to give good yields of the new compound $P_2(CH_3)_4$ will be described in a later paper chiefly concerning this substance. In general, it appears that R_2NPR_2'-type compounds will be key substances in a new approach to alkylphosphine chemistry.

Experimental Part

Synthesis of Dimethylaminodichlorophosphine.—A solution of 6.3 moles of $(CH_3)_2NH$ in an equal volume of dry ether was added slowly to 3.6 moles of PCl_3 in five volumes of ether. The yield of $(CH_3)_2NPCl_2$ was 2.4 moles or 76% based on the amine. Its b.p. was observed as 150°; m.w. of satd. vapor, 154 (calcd., 146). The chloride analysis (Volhard method after hydrolysis) gave 48.4%; calcd., 48.6%. Further characterization was not to the main purpose.

Synthesis of Dimethylaminodimethylphosphine.—The first preparation of $(CH_3)_2NP(CH_3)_2$ began with a 70-g. sample (0.48 mole) of $(CH_3)_2NPCl_2$ in 650 ml. of diethyl ether, in a flask filled with dry nitrogen. A solution of 1.1 moles of CH_3MgBr in 400 ml. of ether was added during 15 minutes, with cooling at −78° except when the mixture became too viscous for the operation of the Hershberg stirrer. However, in later runs it was found that temperatures as high as −16° could be allowed, with improved convenience and no serious loss of yield. After further stirring for an hour at room temperature, the mixture was refluxed for 90 minutes, thus loosening the tacky precipitate. The yellow solution was siphoned off through a dipped-in Soxhlet thimble, and the colorless liquid $(CH_3)_2NP(CH_3)_2$ was isolated by column-distillation. The final purification of small samples was done by high-vacuum fractional condensation (trapped out at −50°, but passing −40°) until 1% first and last fractions showed the same vapor tension (12 mm.) at 0°. The yield from the initial experiment was 25 g., representing 48% of the $(CH_3)_2NPCl_2$.

Methylation at the P–N Bond.—Better yields of the aminophosphine $(CH_3)_2NP(CH_3)_2$ are not easily obtained

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

(3) A. B. Burg, *Chem. Eng. News*, **34**, 2124 (1956).

(4) R. I. Wagner and A. B. Burg, THIS JOURNAL, **75**, 3871 (1953).

(5) G. S. Harris, *Proc. Chem. Soc.*, 119 (1957).

because the Grignard reagent attacks the P–N bond almost as easily as the P–Cl bond. A hint of this effect came in an early experiment in which the $(CH_3)_2NPCl_2$ was added to the CH_3MgBr (rather than *vice versa*), and the yield of $(CH_3)_2NP(CH_3)_2$ was only 10%. More directly, a 475-mg. sample (4.55 mmoles) of $(CH_3)_2NP(CH_3)_2$ reacted as soon as it was mixed with 18 mmoles of CH_3MgBr in 12 g. of di-*n*-butyl ether, and after 1 hr. at 35° the yield of $P(CH_3)_3$ was 216 mg. (62%, based upon the aminophosphine).

This easy replacement of the $(CH_3)_2N$ group by CH_3 led to the hypothesis that some of the $(CH_3)_2NPCl_2$ was converted by the Grignard reagent to some such side product as $(CH_3)_2PCl$, which was not isolated from these reaction mixtures but could be present as a magnesium complex. Accordingly, when two further preparations had given relatively low yields of $(CH_3)_2NP(CH_3)_2$ (31 g. from 0.82 mole of Me_2NPCl_2 and 23 g. from 1.25 moles—36 and 18% yields), the magnesium salt residues were combined and treated in ether with $(CH_3)_2NH$, producing an additional 25 g. of $(CH_3)_2NP(CH_3)_2$. This average 46% improvement of yield was achieved only by refluxing the mixture for some hours, and the reaction might not have been complete; however the result accords with the $(CH_3)_2PCl$ hypothesis. The alternative explanation that the amine only liberated the desired aminophosphine from an Mg-complex does not seem tenable in view of the ease of isolating the initial yield from larger mole proportions of magnesium salts.

Attempts to make $(CH_3)_2PCl$ (or an Mg-complex of it) directly from $PCl_3 + CH_3MgBr$ gave mostly $P(CH_3)_3$, and treatment of the magnesium salt residues with $(CH_3)_2NH$ gave only a 3.6% yield of $(CH_3)_2NP(CH_3)_2$. The aminolysis indicated unused PCl_3 by giving a 12% yield of $[(CH_3)_2N]_3P$, which was identified by comparison of its physical properties with an authentic sample and by the use of 3.08 mmoles of CH_3I to convert 3.076 mmoles of it to the white solid adduct $[(CH_3)_2N]_3PCH_3I$.

Synthesis and Properties of the Tris-amino-phosphine.—The compound $[(CH_3)_2N]_3P$ was made more directly by adding an ether solution of 206 g. (1.5 moles) of PCl_3 to 442 g. (9.8 moles) of $(CH_3)_2NH$ in ether, during 90 minutes. It was then possible to isolate 180 g. (73% yield) of the desired compound. The pure product has a normal b.p. of 163.5°; vapor tension 2.8 mm. at 20°; liquid density 0.911 at 0°.

Ether solutions of $[(CH_3)_2N]_3P$ and CH_3MgBr showed a heat of mixing (complex formation) but no group-exchange during 8 hr. of refluxing. Pyridine was used to precipitate the CH_3MgBr, and 80% of the original tris-amino-phosphine was recovered; there was no yield of $(CH_3)_2NP(CH_3)_2$ at all. In another experiment the conditions were the same except that di-*n*-butyl ether was the solvent, and three-fourths of it was distilled off (at 142°); but again there was no yield of $(CH_3)_2NP(CH_3)_2$.

Physical Properties of Dimethylaminodimethylphosphine.—The m.p. of pure $(CH_3)_2NP(CH_3)_2$ was observed as −97°. The vapor tensions shown in Table I represent two separately purified samples, the second of which is indicated by the asterisk. The point at 99.3° was determined by a quick method whereby the liquid sample acted as a null manometer against one atmosphere pressure of dry nitrogen, thus avoiding a tendency of the substance to decompose into more and less volatile products on standing in contact with mercury at temperatures above 60°. The equation $\log_{10} p_{\text{mm.}} = -(2043/T) + 1.75 \log_{10} T - 0.004495T + 5.5393$ was derived from the points below 60°, indicating the normal b.p. as 99.4° and the Trouton constant as 20.9_0 cal./deg. mole.

TABLE I

VAPOR TENSIONS OF $(CH_3)_2NP(CH_3)_2$

t (°C.)	$p_{\text{mm.}}$ (obsd.)	$p_{\text{mm.}}$ (calcd.)	t	$p_{\text{mm.}}$ (obsd.)	$p_{\text{mm.}}$ (calcd.)
−9.1*	7.07	7.14	34.2	73.14	73.15
0.00*	12.53	12.47	38.6*	89.2	89.0
10.3	22.30	22.37	40.7	97.5	97.4
15.5	29.54	29.51	47.7	129.7	130.6
19.0	35.6	35.3	49.0	138.2	137.6
25.0_5*	47.8	47.7	59.1_5*	205.4	204.4
28.8	56.8	57.0	99.3*	757.0	757.4

Proof of the Formula.—The molecular weight of the purified aminophosphine, determined by measuring the density of the half-saturated vapor at 70°, was 106.7; calcd. for $(CH_3)_2NP(CH_3)_2$, 105.1. A 0.959-mmole sample was hydrolyzed by 1.008 mmoles of water, during 72 hr. at room temperature, yielding 0.955 mmole of nearly pure dimethylamine in accord with the equation

$$(CH_3)_2NP(CH_3)_2 + HOH \longrightarrow (CH_3)_2NH + (CH_3)_2PHO$$

At this point there was a slight trace of dimethylphosphine contaminating the amine (vapor tension 554 mm. at 0°; true value, 562); and after the slightly volatile product had been heated for 8 hr. at 80° with the amine vapor it was possible to isolate 0.12 mmole of dimethylphosphine (vapor tension 334 mm. at 0°; true value, 338). The reaction here presumably was $2(CH_3)_2PHO \rightarrow (CH_3)_2PH + (CH_3)_2POOH$, the latter doubtless forming a phosphonium salt to some extent.

The Methiodide and Mercuric Methiodide Adducts.—A further check of the formula came from the formation and partial analyses of the methiodide $(CH_3)_2NP(CH_3)_2{\cdot}CH_3I$ and the mercuric complex $(CH_3)_2NP(CH_3)_3HgI_3$. The former was precipitated from an ether solution of the aminophosphine by adding methyl iodide. It was recrystallized from an ethanol–ether mixture and analyzed by the Volhard method for iodide: found, 51.27%; calcd., 51.37%. The phosphorus analysis (using the Simmons–Robertson method)[6] gave 12.43%; calcd., 12.54. This methiodide melted with decomposition in the range 315–320°. The mercury complex was made by adding mercuric iodide to the methiodide in ethanol. The light-yellow precipitate was dried at 100° and observed to melt above 300° with decomposition. The hydrolysis of a 59.5-mg. sample, using 0.244 *N* NaOH at 100°, liberated iodide ions amounting to 36.28% (calcd., 36.18). The dimethylamine was distilled off and converted to 6.9 mg. of $(CH_3)_2NH_2Cl$ (calcd., 6.88 mg.; m.p. 172°; mixed m.p. same). This quantitative recovery of the $(CH_3)_2N$ groups from the mercury complex showed that the methiodide was formed by attachment of the CH_3^+ groups exclusively to P rather than to N.

Preparation of Dimethylchlorophosphine.—The reaction

$$(CH_3)_2NP(CH_3)_2 + 2HCl \longrightarrow (CH_3)_2NH_2Cl + (CH_3)_2PCl$$

occurs almost quantitatively at low temperatures. Samples of $(CH_3)_2NP(CH_3)_2$ (4.350 mmoles) and HCl (8.704 mmoles) were condensed together in a vertical tube attached to the high-vacuum system and warmed to −78°, below which a vigorous reaction occurred. After warming to room temperature, the volatile product was removed and weighed as 408.2 mg., corresponding to a 97% yield of $(CH_3)_2PCl$. It was subjected to high-vacuum fractional condensation, passing a trap at −35° and condensing out at −45°. Scarcely a trace of material was trapped at −35°, and what passed the −45° trap was almost the same as the main sample. The solid by-product was analyzed for chloride (Fajans method): found, 4.395 mmoles; calcd. for the predicted $(CH_3)_2NH_2Cl$, 4.350.

These results would indicate a fairly clean production of $(CH_3)_2PCl$ in accord with the equation; however, the yield was not quite 100% and the product had a low molecular weight and a broad melting range. There were also inconsistencies in the preliminary vapor tension values. It appeared that both $(CH_3)_2NP(CH_3)_2$ and $(CH_3)_2PCl$ had been retained to a slight extent in the solid; and a separate experiment showed that these react vigorously together to form a non-volatile adduct which reacts with HCl to make less than a quantitative yield of $(CH_3)_2PCl$. Thus in the main experiment a trace of HCl contaminated the volatile product; and the reason that fractional condensation failed to remove it was found in another experiment showing the existence of a very unstable HCl adduct. At −78°, $(CH_3)_2PCl$ held an equal proportion of HCl in non-volatile form, and only one-third of the HCl could be recovered by fractional condensation methods. The remaining mixture was a little more volatile at 0° than $(CH_3)_2PCl$ and melted in a slightly higher range.

These facts made it possible to plan the preparation of pure $(CH_3)_2PCl$: by the use of more $(CH_3)_2NP(CH_3)_2$ than required by the equation, the HCl was entirely used up and the excess $(CH_3)_2NP(CH_3)_2$ could not act as a volatile impurity in the $(CH_3)_2PCl$ because the adduct $(CH_3)_2NP(CH_3)_2{\cdot}(CH_3)_2PCl$ is too stable and quite non-volatile. The

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

actual experiment employed 5.284 mmoles of $(CH_3)_2NP(CH_3)_2$ and 7.912 mmoles of HCl. The combination occurred in a 50-ml. vertical reaction tube attached to the high-vacuum system, with slow warming from −100° to room temperature. The volatile product now had physical properties indicative of purity; for example, the molecular weight of the 80% saturated vapor was measured as 97.9; calcd., 96.5.

Numerous earlier attempts to make $(CH_3)_2PCl$ by the thermal dissociation of $(CH_3)_3PCl_2$—a method reported by Plets for other R_2PCl compounds[7]—had led only to a non-volatile brown solid, HCl, PCl_3 and all of the chloromethanes. Once, however, we obtained a yield of $(CH_3)_2PCl$ representing a little less than 2% of the phosphorus. It was identified by its mol. wt. (obsd., 97.2; calcd., 96.5), its vapor tension of 34 mm. at 0° and a chloride analysis (found, 37.1%; calcd., 36.7).

Physical Properties of Dimethylchlorophosphine.—The vapor tensions of pure solid $(CH_3)_2PCl$, shown in Table II, determined the equation $\log_{10}p_{\text{mm.}} = 12.1408 - 2887/T$.

TABLE II

VAPOR TENSIONS OF SOLID $(CH_3)_2PCl$

t (°C.)	−39.8	−34.0	−27.4	−18.6	-12.2_5	−5.5
$p_{\text{mm.}}$ (obsd.)	0.57	1.19	2.44	6.31	11.92	22.62
$p_{\text{mm.}}$ (calcd.)	0.59	1.17	2.47	6.31	11.91	22.63

It was more difficult to obtain consistent measurements for the liquid, which slowly and irreversibly formed a slightly soluble non-volatile solid on standing. After each measurement the apparatus could be cleared by flaming *in vacuo* to form volatile materials whose constitution cannot yet be inferred. The vapor tension values shown in Table III determine the equation $\log_{10}p_{\text{mm.}} = 7.844 - 1722/T$. This would indicate the normal b.p. as 71°, but since the Trouton constant (22.9 cal./deg. mole) is a little above normal, the true b.p. probably is nearer to 73°.

TABLE III

VAPOR TENSIONS OF LIQUID $(CH_3)_2PCl$

t (°C.)	0.00	2.4	9.4	15.3	19.8_3	21.7	33.1
$p_{\text{mm.}}$ (obsd.)	34.6	39.5	56.6	74.9	91.5	99.5	168.7
$p_{\text{mm.}}$ (calcd.)	34.7	39.4	56.2	74.9	92.6	100.9	166.5

From the two vapor tension equations the heat of fusion is calculated as 5.33 kcal./mole and the m.p. as −2.0°. The directly observed melting range was −1.4 to −1.0°.

Aminolysis of Dimethylchlorophosphine.—Samples of $(CH_3)_2PCl$ (0.437 mmole) and $(CH_3)_2NH$ (0.947 mmole) were measured as gases and allowed to warm together from −78° to room temperature during 8 hr. The excess amine was distilled through a trap at −78° and measured as 0.071 mmole, meaning that 0.876 mmole of the amine had combined (calcd., 0.876). The volatile product trapped out at −78° had a vapor tension of 12.1 mm. at 0°, corresponding to pure $(CH_3)_2NP(CH_3)_2$; weight 42.2 mg., or 0.402 mmole (92.0% of the expected 0.437). The non-volatile product was analyzed for Cl^-: found, 0.437 mmole, strictly in accord with the equation

$$(CH_3)_2PCl + 2(CH_3)_2NH \longrightarrow (CH_3)_2NP(CH_3)_2 + (CH_3)_2NH_2Cl$$

This result is a further confirmation of the formula $(CH_3)_2PCl$. It appears that 8% of the expected $(CH_3)_2NP(CH_3)_2$ remained with the $(CH_3)_2NH_2Cl$—in what form cannot be judged.

Ammonolysis of Dimethylaminodimethylphosphine.—An initial micro-scale experiment showed that ammonia attacks $(CH_3)_2NP(CH_3)_2$ fairly rapidly at room temperature, displacing more than $2(CH_3)_2NH$ per NH_3 used up, and forming polyphosphino-amines. For more accurately quantitative results, 2.3725 g. (22.57 mmoles) of $(CH_3)_2NP(CH_3)_2$ and 53.2 mg. (3.13 mmoles) of NH_3 were heated for 22 hr. in a 100-ml. sealed tube at 46°. Then the volatile components were separated by high-vacuum fractional condensation, with U-traps at 0, −23, −112 and −196°. The recovery of NH_3 was 0.50 mmole (used, 2.63) and of $(CH_3)_2NP(CH_3)_2$, 16.60 mmoles (used, 5.97 mmoles). The dimethylamine weighed 268.4 mg. (5.96 mmoles; mol. wt. 45.3 *vs.* calcd. 45.1; vapor tension 556 mm. at 0° *vs.* known value, 562). The yield of almost pure $[(CH_3)_2P]_2NH$ was 273.5 mg. (1.995 mmoles); and after very thorough refractionation, the pure product melted in the range 39–40° and showed a vapor tension of 4.1 mm. at 30° (literature values, m.p. 39.5° and 4.13 mm. at 30°).[4] Thus the over-all reaction balance would require that the slightly volatile oily liquid residue contain 1.98 mmoles of $(CH_3)_2P$ groups and 0.635 N, reasonably interpreted as 0.65 mmole of $[(CH_3)_2P]_3N$. The stoichiometry of the whole experiment is well represented by

$$9(CH_3)_2NP(CH_3)_2 + 4NH_3 \longrightarrow 3[(CH_3)_2P]_2NH + [(CH_3)_2P]_3N + 9(CH_3)_2NH$$

The recovery of some ammonia after exposure to a great excess of the aminophosphine suggested that the reaction is sensibly reversible.

Another approach to this complex equilibrium system was tried in an experiment wherein 3.44 mmoles of $(CH_3)_2NP(CH_3)_2$ and 0.479 mmole of $[(CH_3)_2P]_2NH$ reacted partially during 20 hr. at 105–130° to form 0.564 mmole of $(CH_3)_2NH$ and 0.216 mmole of $[(CH_3)_2P]_3N$. The presence of 1.1 mg. (0.068 mmole) of NH_3 again indicated the reversibility of the original ammonolysis.

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(7) V. M. Plets, Dissertation, Kazan, 1938, cited by G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, New York, N. Y., 1950, p. 47.

[CONTRIBUTION NO. 1467 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Hemoglobin Studies. I. The Combination of Carbon Monoxide with Hemoglobin and Related Model Compounds

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The nature of binding of carbon monoxide to hemoglobin, heme and Fe(II)-dicysteinate was studied by means of infrared and magnetic measurements. The formation constant of carbonmonoxyheme was determined and compared to that of carboxyhemoglobin. A possible cause for the unusual resistance of hemoglobin derivatives toward oxidation by molecular oxygen was proposed.

Although it has long been well-known that hemoglobin and myoglobin combine reversibly with molecular oxygen, whereas aqueous solutions of free heme do not, it appears that no satisfactory explanation has yet been proposed to account for this important difference in their chemical property. The mere formation of a coördination bond between a donor group of globin and the ferrous iron in heme is clearly inadequate to prevent the irreversible oxidation of the latter by molecular oxygen, for the ferrohemochromogens formed by combining heme with ammonia, pyridine, imida-

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