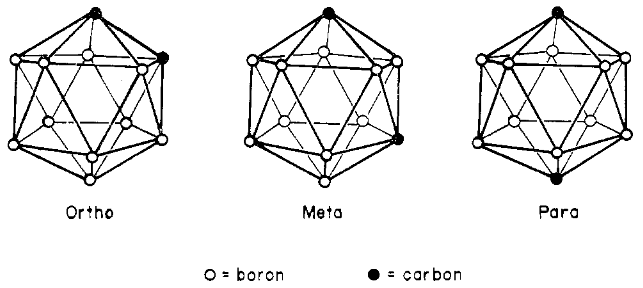

Figure 1.—Structures of the dicarbadecaboranes (hydrogen not shown).

Experimental

Very pure samples of the dicarbadecaboranes were obtained through the courtesy of Dr. T. L. Heying of the Olin Research Center, New Haven, Conn. The benzene employed as solvent was dried by refluxing over potassium and then was distilled and stored over molecular sieves. Duplicate runs were made for each dicarbadecaborane at four different dilutions. All manipulations necessary in preparing a solution were carried out in a glove bag under an atmosphere of dry nitrogen. The dielectric constants of the solutions were measured by the heterodyne-beat oscillator method using a Model DM 01 Dipolmeter with a Type DFL 1 cell.[5] All measurements were made at 25°.

Results

The dipole moments given in Table I were calculated using a modification of the Guggenheim method.[6] The errors indicated are experimental. There are possible errors of up to 10% inherent in the method of calculation.

TABLE I

DIPOLE MOMENTS OF THE DICARBADECABORANES

Compound	Slope $\Delta\epsilon/w$[a]	μ[b], D.
o-$B_{10}H_{10}C_2H_2$	15.33	4.53 ± 0.05
m-$B_{10}H_{10}C_2H_2$	6.07	2.85 ± 0.05
p-$B_{10}H_{10}C_2H_2$	0.00	0.00

[a] Experimental value of slope. $\Delta\epsilon$ is the difference of the dielectric constants of the solutions and benzene, and w is the weight fraction of solute. [b] Calculated from $\mu^2 = (27kT/4\pi N)\cdot(1/d_1(\epsilon_1 + 2)^2)(\text{slope } \Delta\epsilon/w - \text{slope } \Delta n^2/w)M_2$. The contribution of the electronic polarization has been assumed to be negligible when compared to the total polarization because in all cases the slope $\Delta n^2/w$, as measured by an Abbé refractometer, was found to be zero.

Discussion

The values for the dipole moments obtained are in good accord with the structures which have been assigned. The variation in dipole moments for the dicarbadecaboranes shows the same trend as is found in going from the *ortho* to the *para* isomers of disubstituted benzene derivatives. It is of interest also to compare the dicarbadecaboranes with decaborane, whose structure is based on an incompleted boron icosahedron. Decaborane has a dipole moment of about 3.4 D., this being consistent with its open asymmetric structure. Since dicarbadecaboranes are closed icosahedral structures, the dipole moments we have observed indicate fairly large B–C bond moments.

Acknowledgments.—We are indebted to the National Science Foundation and the Advanced Research Projects Agency for financial support for this research.

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[5] Wissenschaftlich-Technische Werkstätten Gmbh., Weilheim/obb., Germany. Kahl Scientific Instrument Corp., El Cajon, Calif.

[6] (a) J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955; (b) F. Oehme and H. Wirth, "The Determination of the Molecular Dipole Moment," Kahl Scientific Instrument Corp., El Cajon, Calif.; (c) J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950); (d) E. A. Guggenheim, *ibid.*, **47**, 573 (1951).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

The Chloramination of Bis(2,2-dimethylhydrazino)phosphines

BY HARRY H. SISLER AND JOSEPH WEISS

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It has recently been established that mono(hydrazino)phosphines react with chloramine to yield aminohydrazinophosphonium salts[1] in which the chloramine nitrogen has become attached to the phosphorus atom, *e.g.*, $[(C_6H_5)_2P(NH_2)[NHN(CH_3)_2]]^+[Cl]^-$. The nitrogen atoms in the mono(hydrazino)phosphines appear to be inert to the attack of the chloramine molecule under the usual chloramination conditions. Further, even in the hydrazinophosphine oxide in which the attachment of an oxygen atom to the phosphorus atom prevents amination of the phosphorus atom, no attack of the hydrazino nitrogen atoms occurs.

In view of the well-known susceptibility of the hydrazine N–N linkage to destructive action by chloramine,[2] the above facts are, to say the least, surprising. We were, therefore, interested in examining this effect further, by studying the chloramination of bis(hydrazino)phosphine derivatives. The present communication reports the results of studies of the reactions of bis(2,2-dimethylhydrazino)phenylphosphine and of bis(2,2-dimethylhydrazino)methylphosphine with the gaseous mixture of chloramine, excess ammonia, and nitrogen obtained by the Sisler–Mattair process.[3,4] The chloramination of bis(2,2-dimethylhydrazino)phenylphosphine oxide was likewise attempted.

Experimental

Materials.—Phenyldichlorophosphine, Victor Chemical Co., practical grade, was purified as described earlier.[5] Methyldichlorophosphine, F.M.C. Corp., industrial grade, was distilled in a vacuum line prior to use. Phenylphosphonic dichloride, Victor Chemical Co., practical grade, was distilled under vacuum; b.p. 88° at 1 mm. 1,1-Dimethylhydrazine, Eastman Kodak, practical grade, was refluxed over calcium hydride for 48 hr. and then distilled from it under dry nitrogen; b.p. 63–64° at

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[1] R. P. Nielsen, J. F. Vincent, and H. H. Sisler, *Inorg. Chem.*, **2**, 760 (1963).

[2] F. N. Collier, H. H. Sisler, J. G. Calvert, and F. Hurley, *J. Am. Chem. Soc.*, **81**, 6177 (1959).

[3] R. Mattair and H. H. Sisler, *ibid.*, **73**, 1619 (1951).

[4] H. H. Sisler, F. T. Neth, R. S. Drago, and D. Young, *ibid.*, **76**, 3906 (1954).

[5] H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

760 mm. Triethylamine, Eastman Kodak, practical grade, was refluxed over calcium hydride for 24 hr. and then distilled from it under dry nitrogen; b.p. 88–89° at 760 mm. Solvents such as chloroform and benzene were refluxed over calcium hydride until dry, distilled, and stored in a nitrogen-filled dry bag in capped bottles.

The gaseous mixture of chloramine and ammonia was produced by the gas phase reaction of chlorine with ammonia as previously described.[3,4] The gas flow rates were such that the input mole ratio $NH_3:N_2:Cl_2$ was about 12:3:1 and the production rate of chloramine was approximately 0.1 mole/hr.

Analyses.—C, H, N, and P analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn.; chloride analyses were performed by the Volhard method after alkaline hydrolysis of the samples.

Bis(2,2-dimethylhydrazino)phenylphosphine.—This compound was prepared in 16% yield by the addition of 0.78 mole of phenyldichlorophosphine over a period of 1 hr. to a benzene solution of 1.95 moles of 1,1-dimethylhydrazine and 1.56 moles of triethylamine at 0°. This was followed by filtration of the insoluble triethylammonium chloride formed and washing of this solid with benzene. Manipulations were performed in a nitrogen-filled dry bag. Solvent was removed from the combined filtrate and washings under vacuum and the product obtained by vacuum sublimation of the residual oil at 55°; m.p. 65–67.5°. The melting point and infrared spectrum agree with that previously reported[6] for this compound.

Bis(2,2-dimethylhydrazino)methylphosphine.—Bis(2,2-dimethylhydrazino)methylphosphine was prepared by the addition of 0.2 mole of methyldichlorophosphine over a period of 1 hr. to a benzene solution of 0.4 mole of 1,1-dimethylhydrazine and 0.5 mole of triethylamine at −5° with constant stirring. A positive pressure of dry nitrogen was maintained throughout. When the addition was complete, the insoluble triethylammonium chloride formed was filtered off and the filter cake was washed with benzene. Solvent and unreacted starting materials were distilled under vacuum from the combined filtrate and washings, leaving behind a white crystalline solid and a small amount of an oil. Bis(2,2-dimethylhydrazino)methylphosphine (14% of theory) was obtained from this mixture by vacuum sublimation at 35° in a closed system under a self-generated pressure of approximately 25 mm. of 1,1-dimethylhydrazine. *Anal.* Calcd. for $CH_3P[NHN(CH_3)_2]_2$: C, 36.58; H, 10.42; N, 34.11; P, 18.84. Found: C, 36.43; H, 10.31; N, 33.96; P, 18.99. The infrared spectrum shows major absorption bands at 3300, 1275, 1209, 1150, 1004, and 869 cm.$^{-1}$.

Bis(2,2-dimethylhydrazino)phenylphosphine Oxide.—A 46.2% yield of bis(2,2-dimethylhydrazino)phenylphosphine oxide was obtained by the addition with stirring of 0.03 mole of phenylphosphonic dichloride over a period of 0.5 hr. to a benzene solution of 0.07 mole of 1,1-dimethylhydrazine and 0.08 mole of triethylamine at 0°. The reaction mixture was heated to 50° and stirring was continued for another hour, the system being all the while maintained under a positive pressure of dry nitrogen. The insoluble triethylammonium chloride formed during the reaction was filtered off and then washed with benzene. The filtrate was cooled to 6°, whereupon a crop of white crystals was deposited. These were recrystallized from benzene. The infrared spectrum shows an absorption at 1128 cm.$^{-1}$ characteristic of tetracoordinated phosphorus to which one phenyl group is attached; m.p. 166–167.5°. *Anal.* Calcd. for $C_6H_5P(O)[NHN(CH_3)_2]_2$: C, 49.62; H, 7.84; N, 23.10; P, 12.78. Found: C, 49.51; H, 7.80; N, 22.99; P, 12.52.

Oxidation of Bis(2,2-dimethylhydrazino)phenylphosphine.—Bis(2,2-dimethylhydrazino)phenylphosphine (0.0135 mole) was dissolved in 60 ml. of benzene and dry oxygen gas was passed through the solution for 12 hr. at 50°. Solvent removal under vacuum left an oil together with some dispersed solid material. Vacuum sublimation of this residue yielded starting material on the cold finger and a hard, white residue. The residue was dissolved in warm benzene and 12% of the theoretical quantity of oxide was recovered by recrystallization from benzene–*n*-hexane mixtures. This product was identical with that obtained from the reaction with phenylphosphonic dichloride described above.

Chloramination of the Bis(2,2-dimethylhydrazino)phosphines.—Bis(2,2-dimethylhydrazino)phenylphosphine (0.0159 mole) was dissolved in 100 ml. of benzene, and the effluent from the chloramine generator was passed through the solution for 45 min. A white precipitate formed immediately. This was filtered, dried, and extracted with chloroform to separate the ammonium chloride. The chloroform was evaporated under vacuum and an 80% yield of white crystals obtained. The infrared spectrum shows the absorption at 1128 cm.$^{-1}$ characteristic of a tetracoordinate phosphorus atom to which a phenyl group is attached; m.p. 178–181° dec. *Anal.* Calcd. for $[C_6H_5P(NH_2)[NHN(CH_3)_2]_2]^+[Cl]^-$: C, 43.30; H, 7.57; N, 25.23; P, 11.16; Cl, 12.79. Found: C, 42.61; H, 7.65; N, 24.75; P, 10.81; Cl, 12.54.

Bis(2,2-dimethylhydrazino)methylphosphine (0.01 mole) was dissolved in 75 ml. of dry benzene and treated as was the phenyl analog. The white precipitate that formed was boiled with 300 ml. of chloroform and the resultant suspension filtered. Removal of the chloroform from the filtrate under vacuum left behind a crop of white crystals. These were washed with a small amount of chloroform and dried under vacuum. In contrast to the behavior of a number of similar nitrogen–phosphorus species, this compound does not form an adduct with dimethylformamide; yield 90%; m.p. 196–198° dec. *Anal.* Calcd. for $[CH_3P(NH_2)[NHN(CH_3)_2]_2]^+[Cl]^-$: C, 27.82; H, 8.85; N, 32.52; P, 14.36; Cl, 16.46. Found: C, 27.62; H, 8.66; N, 32.35; P, 14.14; Cl, 16.78.

Hydrolysis of the Bis(2,2-dimethylhydrazino)aminophosphonium Chlorides.—The bis(2,2-dimethylhydrazino)aminophosphonium chlorides prepared are water-soluble salts possessing an ionic chlorine atom which can be rapidly precipitated as silver chloride immediately after solution in water before hydrolysis of the cation is appreciable. Basic hydrolysis liberates both ammonia and 1,1-dimethylhydrazine. These bases were isolated as their hydrochlorides following treatment of the hydrolysis reaction mass with hydrochloric acid and separation of the salts with absolute ethanol.

Attempted Chloramination of Bis(2,2-dimethylhydrazino)phenylphosphine Oxide.—The effluent from the chloramine generator was passed through a solution containing 0.0117 mole of the oxide in 70 ml. of benzene at 60° for 0.5 hr. A moderate amount of white solid precipitated from solution during this interval. The suspension was filtered, the filter cake washed with benzene, and the solvent removed from the filtrate under vacuum. Unreacted oxide was isolated by recrystallization of the residue from benzene–*n*-hexane mixtures. The precipitated material was analyzed and found to consist of starting material and ammonium chloride. The infrared spectrum of the precipitated material agrees with this conclusion. Vacuum sublimation of the solid yielded only ammonium chloride on the cold finger and no trace of dimethylammonium chloride or of 1,1-dimethylhydrazinium chloride could be detected.

Pyrolysis of Bis(2,2-dimethylhydrazino)aminophenylphosphonium Chloride.—Pyrolysis of bis(2,2-dimethylhydrazino)aminophenylphosphonium chloride at 200° *in vacuo* led to a 23% loss in weight. The products were a small amount of nitrogen, a distillate which was liquid at −76°, and a residual glass. Vapor phase chromatographic analysis of the distillate on a 9-ft. silicone–elastomer-on-Chromosorb P column at various temperatures indicated the presence of ammonia, 1,1-dimethylhydrazine, and a very small amount of a basic substance, as yet unidentified, which however was not dimethylamine, hydrazine, or methylamine. The distillate was neutralized with hydrochloric acid and the ammonium chloride and 1,1-dimethylhydrazinium chloride formed were isolated as described above. The pyrolysis residue was extracted with chloroform to yield a solid residue of ammonium chloride and a brown solution. Solvent removal

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[6] E. M. Winyall, M.S. Thesis, University of Florida, 1964; E. M. Winyall and H. H. Sisler, *Inorg. Chem.*, **4**, 655 (1965).

from this solution left a chloride-free material which exhibited an average molecular weight of 950 (Rast method).

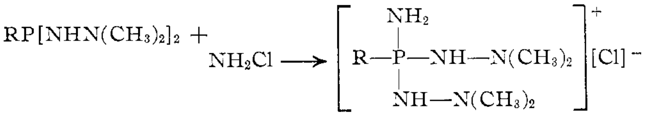
The infrared spectrum of this material contains the broad absorption band characteristic of the phosphonitrilic linkage in the region 1000–1420 cm.$^{-1}$. Thus it appears that this material contains phosphonitrilic species and is probably a mixture of a variety of such species. Thin layer chromatography on silica, as well as fractional crystallization from chloroform, failed to effect a separation of the phosphonitrilic components of the mixture.

Treatment of this material with water transforms it to a tan powder, which when dry exhibits nonwetting properties in that it forms a dry film on a water surface and is wetted only with difficulty and has an average molecular weight of 900 (Rast method) and an infrared spectrum very similar to that of the parent material. Again, thin layer chromatography on silica and fractional crystallization from chloroform or benzene failed to effect a separation of the components present.

Pyrolysis of bis(2,2-dimethylhydrazino)aminomethylphosphonium chloride under identical conditions produced a brown glassy solid residue which was essentially insoluble in chloroform or benzene. The infrared spectrum of this material shows a strong broad absorption in the 1000–1420 cm.$^{-1}$ region. This indicates that the presence of a major amount of a mixture of phosphonitrilic materials is highly probable.

Discussion

The results of the experiments described above clearly indicates that the chloramination of the bis(2,2-dimethylhydrazino)phosphines studied may be represented by the equation



$$RP[NHN(CH_3)_2]_2 + NH_2Cl \longrightarrow \left[R{-}\overset{NH_2}{\underset{NH{-}N(CH_3)_2}{P}}{-}NH{-}N(CH_3)_2 \right]^+ [Cl]^-$$

$(R = CH_3 \text{ or } C_6H_5)$

It is thus established that even when two hydrazino groups are attached to the phosphorus atom all of the hydrazino nitrogen atoms are inert to chloramination, even when the phosphorus atom is made unavailable for reaction with chloramine by formation of the bis(hydrazino)phosphine oxide. In the reaction of bis(2,2-dimethylhydrazino)phenylphosphine oxide with the ammonia–chloramine mixture the infrared spectrum of the resultant products plus the fact of the recovery of the starting material indicate that the only change which occurs is the formation of ammonium chloride (and presumably nitrogen) from the reaction of chloramine and ammonia. It is probable that this reaction may have been catalyzed by the presence of the phosphine oxide.

The pyrolysis of bis(2,2-dimethylhydrazino)aminophenylphosphonium chloride obtained from the chloramination of the corresponding bis(hydrazino)phosphine yields ammonia, 1,1-dimethylhydrazine, a small amount of nitrogen gas, and a very small amount of an unidentified basic nitrogen compound which, however, is not methylamine, dimethylamine, or hydrazine. The glassy residue is shown by its infrared spectrum and composition to probably contain a major amount of a mixture of phosphonitrilic derivatives with an average molecular weight of 950 (Rast method) plus some ammonium chloride. A similar material (most likely polymeric) was obtained from the pyrolysis of bis(2,2-dimethylhydrazino)aminomethylphosphonium chloride.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON,
AND THE DEPARTMENT OF PHYSICAL SCIENCES,
UNIVERSITY OF IDAHO, MOSCOW, IDAHO

Difluoroaminooxyperfluoromethane, CF_3ONF_2

BY JEAN'NE M. SHREEVE, LEONARD CLINTON DUNCAN,
AND GEORGE H. CADY

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The colorless, gaseous compound, CF_3ONF_2, has been prepared by the reaction of CF_3OF with N_2F_4 and by the basic hydrolysis of $CF_3OSF_4NF_2$.

A mixture of CF_3OF and N_2F_4 at initial pressures of 251 and 130 mm., respectively, in a 1.2-l. nickel vessel was held at room temperature, about 23°, for 21 hr. Products which were identified through infrared spectra after separation by fractional codistillation included CF_4, NF_3, COF_2, and SiF_4 (which must have formed in the glass vacuum system for handling the material), as well as unreacted CF_3OF and N_2F_4. Two other compounds found were CF_3ONF_2 and a small amount of an unidentified product with a boiling point near room temperature.

When 223 mm. of CF_3OF (contaminated with COF_2 and CF_4) and 209 mm. (36 mmoles) of N_2F_4 were mixed in a 3.2-l. Pyrex bulb and irradiated through a quartz finger for 3 hr., about 13 mmoles of CF_3ONF_2 was formed. A Hanau high-pressure ultraviolet lamp, Type 81, was used. Other components of the product mixture included NF_3, $(NO)_2SiF_6$, and unreacted starting materials. Although Pyrex glass vessels may be used for the preparation, it is more convenient to use metal vessels without ultraviolet irradiation to preclude the formation of large quantities of $(NO)_2SiF_6$.

Partial conversion to CF_3ONF_2 occurred, as was indicated by an infrared spectrum of the residual gases, when a sample of gaseous $CF_3OSF_4NF_2$[1] was held for 3 days at room temperature in a Pyrex glass flask which contained an excess of 1 *M* aqueous sodium hydroxide solution. When the mixture of gases was then held in contact with 2 *M* NaOH for 2 hr. at about 67°, no $CF_3OSF_4NF_2$ remained, and the gas, after drying, was identified as substantially pure CF_3ONF_2 in a yield greater than 90%.

Difluoroaminooxyperfluoromethane was shown to have an experimentally determined molecular weight

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[1] L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 1045 (1964).