It is interesting to compare the hydridic hydrogen content (a measure of reducing capacity per unit weight) of ethane 1,2-diamineborane with that of other amineboranes which are commercially available[24] (Table I).

TABLE I

ACTIVE HYDROGEN CONTENT OF AMINEBORANES

| No. | Compound | %H (hydridic) |
|---|---|---|
| 1 | Ethane 1,2-diamineborane | 6.83 |
| 2 | Trimethylamineborane | 4.14 |
| 3 | Dimethylamineborane | 5.13 |
| 4 | Pyridineborane | 3.25 |

Thus, ethane 1,2-diamineborane contains 33% more active hydrogen per unit weight than its closest competitor, dimethylamineborane. Comparison with other available products is even more striking. Dimethylamineborane melts at 36° and frequently must be purified from an unstable form (m. 11°) by recrystallization from hot petroleum ether or by vacuum distillation, b. 59–65° at 1–2 mm.[24,28] The advantageous position of ethane 1,2-diamineborane is evident from a consideration of stability, handling difficulties and hydridic hydrogen content.

Ethane 1,2-diamineborane appears to exhibit selectivity and reactivity toward organic functional groups comparable to sodium borohydride. Its solubility in a variety of liquids plus its successful use as an aqueous slurry make it amenable for a variety of reducing reactions under a number of solvolytic conditions. It should prove an interesting addition to the list of complex hydride reducing agents.

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(28) E. Wiberg, A. Bolz and P. Buchheit, *Naturwissenschaften*, **35**, 182 (1948).

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[CONTRIBUTION FROM THE POLYMER STRUCTURE SECTION, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

# Preparation and Thermal Stability of Tetrakis-(pentafluorophenyl)-silane and Tris-(pentafluorophenyl)-phosphine[1]

BY LEO A. WALL, ROBERT E. DONADIO AND WALTER J. PUMMER

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The completely fluorinated organo-metalloid compounds, tetrakis-(pentafluorophenyl)-silane, tris-(pentafluorophenyl)-phosphine and tris-(pentafluorophenyl)-phosphine oxide have been prepared from pentafluorophenylmagnesium bromide and the appropriate metalloid chloride. The thermal stability of each of these compounds has been compared with that of other aromatic substances. It was found in the case of the phosphine, where coördinating electrons exist on the metalloid atoms, that complete fluorine substitution increases its thermal stability and resistance to oxidation. On the other hand, complete fluorination decreases the thermal stability of the silane.

Pentafluorobromobenzene[2] and pentafluoroiodobenzene[3] have recently been synthesized in this laboratory and also in England.[4] These substances react with magnesium to form nearly typical Grignard reagents.[3,4] Several new compounds have already been prepared[3,4] *via* these reagents, and the synthesis of many more is evidently possible.

Aromatic fluorocarbons are of interest as the basis for new thermally stable liquids and polymers. Before attempting the preparation of the larger molecules that make up such materials, it would be desirable, however, to have thermal decomposition data on the smaller molecules. In this paper we shall describe the synthesis and physical properties of two new compounds—tetrakis(pentafluorophenyl)-silane and tris(pentafluorophenyl)phosphine—and report the results of a qualitative study of the thermal decomposition of these compounds, other aromatic fluorocarbons and related hydrocarbons.

## Experimental[5,6]

**Tetrakis-(pentafluorophenyl)-silane (I).**—This compound is readily formed when silicon tetrachloride is added to an ether solution of the pentafluorophenyl magesnium bromide.[3,4] To the Grignard reagent, prepared from 24.7 g. (0.1 *M*) of pentafluorobromobenzene and 2.43 g. (0.1 g. atom) of magnesium turnings in 50 ml. of anhydrous ether, was added 4.25 g. (0.0025 *M*) of silicon tetrachloride dropwise while cooling by means of an ice-bath. When the addition was completed, the mixture was stirred for 1 hr. more at 0°, refluxed for 3 hr. and finally allowed to come to room temperature overnight. Ice water (25 ml.) was added to the cooled reaction mixture, followed by the addition of 25 ml. of 6 *N* hydrochloric acid. After 0.5 hr. of stirring, the mixture was poured into 100 ml. of *N* hydrochloric acid and filtered. From the 9 g. of brown filter cake, 5.5 g. of I (32% yield) was obtained as white needles by sublimation at 208° (1 mm.). After several recrystallizations from an acetone–benzene mixture, it melted at 248–250°. The infrared absorption spectrum showed peaks at wave lengths 6.57, 7.72, 9.1 and 10.26$\mu$. The remaining 3.5 g. of solid appeared to be inorganic in composition and acid insoluble.

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(1) Based on work sponsored by the Bureau of Aeronautics and the Office of Naval Research, Department of the Navy, Washington, D. C.,

(2) M. Hellmann, E. Peters, W. J. Plummer and L. A. Wall, THIS JOURNAL, **79**, 5654 (1957).

(3) W. J. Pummer and L. A. Wall, *J. Research Natl. Bur. Standards* **63A**, 167 (1959).

(4) E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959).

(5) Chemical analyses were performed by Robert Deardorff of the Analytical Chemistry Section of the National Bureau of Standards.

(6) Melting points were determined with a Fisher Johns apparatus calibrated with pure samples of naphthalene, benzoic acid and dimethylterephthalate.

*Anal.* Calcd. for $C_{24}F_{20}Si$: C, 41.5; F, 54.8; Si, 4.02. Found: C, 41.6; F, 53.6; Si, 4.3.

**Bis-(pentafluorophenyl)-dichlorosilane** (II).—Initial attempts to prepare this compound have so far resulted only in the isolation of further quantities of I. The Grignard reagent was prepared as described previously, except that 49.4 g. (0.2 *M*) of pentafluorobromobenzene, 4.86 g. (0.2 g. atom) of magnesium turnings and 75 ml. of anhydrous ether was used. The Grignard reagent was filtered under a helium atmosphere into a dropping funnel and added dropwise into a solution of 19.8 g. (0.11 *M*) of silicone tetrachloride in 50 ml. of anhydrous ether. The addition required 1.5 hr. After refluxing for 5 hr., the mixture was cooled and again filtered in a helium atmosphere. The brown solid remaining was washed thoroughly with anhydrous ether and filtered again. This solid gave 12 g. (35%) of I, m.p. 247–249°. From the combined ether solutions, only a black tar was obtained, from which no products could be identified. This tarry product was probably a polymer of the desired product.

**Tris-(pentafluorophenyl)-phosphine** (III).—This compound is prepared readily when phosphorus trichloride is added to the Grignard reagent, pentafluorophenylmagnesium bromide, a method similar to that employed by Dodonov[7] for the preparation of triphenylphosphine. The Grignard reagent, pentafluorophenylmagnesium bromide, was prepared in the manner described previously[3] from 30 g. (0.122 *M*) of pentafluorobromobenzene and 2.95 g. (0.122 g. atom) of magnesium turnings in anhydrous ether under an atmosphere of hydrogen. To the dark brown, nearly opaque solution was added dropwise 5.0 g. (0.037 *M*) of phosphorus trichloride in 20 ml. of anhydrous ether. The flask was cooled in an ice-water bath. After addition was complete, the ice bath was removed, and the flask was allowed to stand at room temperature for 15 min. The solution was hydrolyzed with 40 ml. of cold dilute hydrochloric acid. The layers were separated, and the acidic solution was extracted twice with 30 ml. portions of ether. The combined ether solution was dried over anhydrous calcium sulfate and concentrated under reduced pressure to give 13.1 g. of a dark brown solid which emitted a strong match-like odor. Sublimation under reduced pressure in an apparatus heated in an oil-bath from 100 to 130° gave 8.5 g. (39.5%) of III was white needles, m.p. 116–117°.

Infrared spectrum: 6.08μ, 6.57μ (C=C, Ar), 6.78μ (C–P), 10.25μ (C–F). Ultraviolet spectrum: $\lambda_{max}^{CH_3OH}$, 253 mμ ($\epsilon$ = 10,400); $\lambda_{min}^{CH_3OH}$, 241 mμ ($\epsilon$ = 8,900); conc., $2.52 \times 10^{-5}$ *M*, cell, 2 cm.

*Anal.* Calcd. for $C_{18}F_{15}P$: C, 40.6; F, 53.6; P, 5.8. Found: C, 40.3; F, 54.5; P, 5.7.

**Tris-(pentafluorophenyl)-phosphine Oxide** (IV).—This compound can be prepared by the strong oxidation of III. The phosphine (III), 2.0 g. (0.0038 *M*), was placed in a solution of 10 g. of sodium dichromate in 25 ml. of water acidified with 10 ml. of concentrated sulfuric acid and 25 ml. of glacial acetic acid, and the mixture was refluxed for 6 hr., during which time the phosphine slowly dissolved as it was oxidized. The solution was made alkaline with dilute sodium bicarbonate solution and extracted three times with 50-ml. portions of chloroform. The chloroform solution was dried with anhydrous sodium sulfate and evaporated to give approximately 2.0 g. of a white solid (IV), recrystallized from petroleum ether (low boiling) as fine needles, m.p. 169–170°.

Infrared spectrum: 6.08μ, 6.59μ (C=C, Ar); 6.75μ (C–P), 8.15μ (P–O), 10.15μ (C–F). Ultraviolet spectrum: $\lambda_{max}^{CH_3OH}$, 275 mμ ($\epsilon$ = 2,600); $\lambda_{max}^{CH_3OH}$, 250 mμ ($\epsilon$ = 730); conc., $2.74 \times 10^{-4}$ *M*; cell, 1 cm.

*Anal.* Calcd. for $C_{18}F_{15}OP$: C, 39.4; F, 52.0; P, 5.65. Found: C, 39.5; F, 52.9; P, 5.6.

**Thermal Stability.**—The procedure was to seal 0.01 to 0.5 g. of each material in a thick-walled, hard-glass tube of 1–2-mm. i. d., evacuating thoroughly before sealing off the tube. The tube was then heated in a thermostatted furnace at temperatures in the range of 200 to 700° for varying periods of time, 1 to 20 hr. After heating, the condition of the material was noted.

## Discussion

**Physical Properties.**—The melting point (249°) of I is unusually high, since tetraphenylsilane melts at 232°.[8] This large difference is unlike that of other known aromatic fluorocarbons, where the melting points are close to those of their hydrocarbon analogs. For example, diphenyl melts at 69°, as compared to decafluorodiphenyl at 70°[3]; and naphthalene melts at 80°, as compared to decafluoronaphthalene at 86°.[9]

An examination of a Fischer–Hirshfelder model of I suggests that rotation of the phenyl groups about the carbon–silicon bond is hindered by the ortho fluorine atoms to an appreciably greater extent than in the hydrocarbon analog of I. As a result, rotation of a phenyl group in I would require a coöperative action of adjacent phenyl groups, which may account for the higher melting point.

The results of the attempted preparation of bis-(pentafluorophenyl)-silane suggests, as recently reported in the preparation of tetrakis-(trifluorovinyl)-silane,[10] that the first pentafluorophenyl group, upon becoming attached to the silicon, activates the remaining chlorine atoms. There should be no inherent problem in preparing bis-(pentafluorophenyl)-dichlorosilane and hence the poly[bis(pentafluorophenyl)-siloxane], although a less direct procedure may prove more efficient. Further work is planned using improved anhydrous conditions and low ratios of the Grignard reagent to the silicon tetrachloride.

The electron-withdrawing character of the fluorine substituents in III appears to result in a stronger interaction between unshared electron pairs on the phosphorus atom with the pi electrons of the aromatic nuclei than in triphenylphosphine. The compound III is thus more acidic. Thus, unlike triphenylphosphine, III does not form a phosphonium salt with methyl iodide and is converted only through strong oxidation to tris-(pentafluorophenyl)-phosphine oxide (IV). An enhanced resonance state in III is apparent in its ultraviolet spectrum, which exhibits an absorption maximum at 253 mμ ($\epsilon$ = 10,400). Oxidation produces a large bathochromic shift to 275 mμ for the absorption peak of IV ($\epsilon$ = 2,600), indicating but little conjugative interaction of pentafluorophenylphosphoryl groups. These results are in close accord with spectral data obtained for triphenylphosphine and its corresponding oxide, which show absorption maxima at 261 mμ ($\epsilon$ = 11,000) and 266 mμ ($\epsilon$ = 2,410), respectively.[11]

The complete substitution with fluorine increases the melting point of the triphenylphosphine from 79° to 116–117°. This increase is considerably greater than that noted in the silane. The previously suggested explanation may also account for this increase. However, an additional possibility exists here as a result of the extra pair of electrons

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[7] J. Dodonov and H. Medox, *Ber.*, **61**, 907 (1928).

[8] A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 2337 (1954).

[9] B. Gething, C. R. Patrick, M. Stacey and J. C. Tatlow, *Nature*, **183**, 588 (1959).

[10] R. N. Sterlin, I. L. Knunyants, L. N. Pinkina and R. D. Yatsenko, *Izvest. Akad. Nauk S.S.S R.*, 1492 (1959).

[11] H. H. Jaffe and L. D. Freedman, THIS JOURNAL, **74**, 1069 (1952).

on the phosphorus. The inductive effect of the fluorine atoms may decrease the electron density on the phosphorus to such an extent that an appreciable dipole moment is produced which leads to a much greater intermolecular attraction. The melting point, 156°, of triphenylphosphine oxide is also increased 12 degrees by fluorine substitution. Increased hindrance to rotation of the phenyl groups would seem the better explanation here.

**Thermal Stability.**—The thermal decomposition of the newly synthesized compounds I, III, IV, and of decafluorodiphenyl were studied qualitatively. The hydrocarbon analogs, except for that of IV, were also studied. The results are shown in Table I. The relative thermal stability of the compounds appears to be in the order: $(C_6F_5)_2 \geq (C_6H_5)_2 > (C_6H_5)_4Si \geq (C_6F_5)_4Si > (C_6F_5)_3P > (C_6H_5)_3P > (C_3F_5)_3PO$.

It should be emphasized that these experiments were conducted in glass. Even so, perfluorodiphenyl is unchanged until held at 575° for 1 hr. It is believed that, in appropriate metal apparatus, it would show somewhat greater thermal stability than its hydrocarbon analog. Of the aromatic hydrocarbons in general, diphenyl is one of the most thermally stable. We have also studied in a similar manner about forty hydrocarbon aryl silanes without finding any with greater thermal stability than tetraphenylsilane, $[(C_6H_5)_4Si]$, which is considerably less stable than diphenyl.

The effect of the pentafluorophenyl group on the thermal stability undergoes a reversal in direction between the silane and phosphine. The presence of fluorine decreases the stability of the silane but increases the stability of the phosphine. However, the fluorophosphine oxide is less stable than the triphenylphosphine. These phenomena are obviously connected with the pair of coördinating electrons on the phosphine. The trends in the results suggest fairly marked differences in the bond strengths of the Si–C and P–C bonds in these compounds as a result of the fluorine substitution.

Table I

Comparison of Thermal Stabilities

| Compound | M.p., °C. | Heating conditions |  | Condition of sample |
|---|---|---|---|---|
|  |  | Temp., °C. | Time, hr. |  |
| $(C_6F_5)_4Si$ (I) | 249 | 500 | 1 | Charred, not coked |
|  |  | 500 | 2 | Charred, definite etching |
|  |  | 500 | 3 | Coked, etched tube |
| $(C_6H_5)_4Si$ | 232 | 500 | 1 | Yellow color |
|  |  | 500 | 2 | Yellow, decomposition started |
| $(C_6F_5)_2$ | 70 | 325 | 1 | Unchanged |
|  |  | 366 | 1 | Unchanged |
|  |  | 420 | 2 | Unchanged |
|  |  | 500 | 1 | Unchanged |
|  |  | 575 | 1 | Slight coloration |
|  |  | 660 | 1 | Charred |
| $(C_6H_5)_2$ | 69 | 500 | 1 | Unchanged |
|  |  | 500 | 2 | Unchanged |
|  |  | 500 | 3 | Unchanged |
|  |  | 660 | 1 | Tube burst, some decomposition indicated |
| $(C_6F_5)_3P$ (III) | 116–117 | 200 | 20 | Unchanged |
|  |  | 300 | 20 | Slight yellowing |
|  |  | 400 | 6 | Slight yellowing, m.p. 115° |
|  |  | 450 | 3 | Tan crystals, m.p. 110–113° |
|  |  | 450 | 20 | Dark brown oil |
| $(C_6H_5)_3P$ | 79 | 300 | 20 | Unchanged |
|  |  | 400 | 6 | Yellow liquid, some crystals, m.p. 73° |
|  |  | 400 | 20 | Dark brown oil |
| $(C_6F_5)_3OP$ (IV) | 169–170 | 200 | 20 | Unchanged |
|  |  | 300 | 20 | Dark brown oil |

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[Contribution from the Chemical and Metallurgical Division, Sylvania Electric Products, Inc., Towanda, Pennsylvania]

# Phosphates of Cadmium

By R. C. Ropp and R. W. Mooney

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The phosphate, $Cd_5H_2(PO_4)_4(H_2O)_4$, is stable over wide concentration, temperature and pH limits, converting in the presence of ammonia at pH 7.5 or above to one of two forms of cadmium ammonium phosphate hydrate, depending on ammonia concentration. In contrast to earlier results, no other basic phosphates could be precipitated, although cadmium hydroxylapatite was readily prepared by prolonged hydrolysis. A study of the thermal behavior of the compounds by means of differential thermal and thermogravimetric analysis showed that $Cd_5H_2(PO_4)_4(H_2O)_4$ dehydrates readily, losing up to four molecules of water before a change in structure is apparent, thus revealing properties somewhat similar to alkaline-earth hydroxylapatites. The ammonium phosphates form an intermediate $(CdHPO_4)_3 \cdot NH_3$ and finally convert to the pyrophosphate.

## Introduction

The preparation of the cadmium phosphates was explored many years ago by several authors[1–3] who, for the most part, described the forms obtained and a method of precipitation, but gave

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(1) F. Stromeyer, *Schweiggers J.*, **22**, 362 (1818).

(2) A. deShulten, *Bull. soc. chim.*, France, **1**, 472 (1889).

(3) E. H. Miller and R. W. Page, *School Mines Quart.*, **22**, 391 (1900). See also: J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., New York, N. Y., 1940, pp. 658–665.