[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Organosilicon Compounds Containing the *p*-Dimethylaminophenyl Group

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Eleven new organosilicon compounds containing the *p*-dimethylaminophenyl group have been prepared. Several unusual properties of the *p*-dimethylaminophenylsilicon compounds as compared with their phenyl and *p*-tolyl analogs have been noted. (1) They are formed from silicon tetrachloride and the appropriate organolithium compound more slowly than the corresponding phenyl or *p*-tolyl compounds. (2) Tris-(*p*-dimethylaminophenyl)-chlorosilane and tris-(*p*-dimethylaminophenyl)-silane melt unusually high. (3) Tris-(*p*-dimethylaminophenyl)-silane is unusually resistant to hydrolysis by alkali. (4) Tris-(*p*-dimethylaminophenyl)-silanol is unusually resistant to condensation to the disiloxane. (5) Tris-(*p*-dimethylaminophenyl)-silanol reacts with di-*n*-butylamine to give a compound containing a silicon to nitrogen bond, while other silanols have not been found to do this.

In the course of studies on the absorption spectra of organosilicon compounds,[1] it was found necessary to prepare some compounds in which the *p*-dimethylaminophenyl group is attached to silicon. When three equivalents of *p*-dimethylaminophenyllithium were added to silicon tetrachloride with good cooling in the usual manner[2] and the mixture hydrolyzed, only bis-(*p*-dimethylaminophenyl)-silanediol was obtained.[3] This unexpected result was found to be due to the fact that *p*-dimethylaminophenyllithium reacts with arylchlorosilanes at a much slower rate than do the aryllithiums previously reported in the literature. If the course of the reaction is followed with Color Test I,[4] it is found that three equivalents of phenyl- or *p*-tolyllithium react with silicon tetrachloride almost instantaneously at 0° while three equivalents of *p*-dimethylaminophenyllithium require 48 hours of refluxing in ether before the color test becomes negative. Under these conditions, satisfactory yields of tris-(*p*-dimethylaminophenyl)-chlorosilane and tris-(*p*-dimethylaminophenyl)-silanol can be obtained. Similarly, in order to complete the reaction between silicon tetrachloride and four equivalents of *p*-dimethylaminophenyllithium, their ether solution must be refluxed for 60 hours.

When allowance was made for this slower rate of reaction, no difficulty was experienced in preparing most of the *p*-dimethylaminophenylsilicon compounds listed under Experimental. However, when silicochloroform was refluxed with three equivalents of *p*-dimethylaminophenyllithium, a solid melting at 157° was obtained, which gave a negative test for the Si–H linkage (potassium hydroxide in piperidine[5]). Since most triarylsilanes give this test and melt about 100° lower, some doubt was entertained as to the identity of the product. Silicon and nitrogen analyses could not distinguish between tris-(*p*-dimethylaminophenyl)-silane, tris-(*p*-dimethylaminophenyl)-silanol and hexakis-(*p*-dimethylaminophenyl)-disiloxane, but since the material gave no gas on treatment with methyllithium, and had a molecular weight corresponding to a monosilicon compound, it was assumed to be tris-(*p*-dimethylaminophenyl)-silane. This was confirmed when it was found that the same compound was obtained if tris-(*p*-dimethylaminophenyl)-chlorosilane was reduced with lithium aluminum hydride,[6] and that treatment of the product with 2% potassium hydroxide in absolute ethanol at 60° gave a gas and tris-(*p*-dimethylaminophenyl)-silanol.

In order further to confirm that the compound melting at 157° is the triarylsilane and not the hexaaryldisiloxane, several attempts were made to prepare hexakis-(*p*-dimethylaminophenyl)-disiloxane. When tris-(*p*-dimethylaminophenyl)-silanol was treated with concentrated formic or acetic acid (a method which has given excellent yields of disiloxanes with triphenyl-, tri-*p*-tolyl-, and tri-*p*-chlorophenylsilanols[7]) only blue, glassy, polymeric materials were obtained. Probably the silanol was decomposed by the strong acid.[8] Basic condensing agents were equally unsuccessful, since when tris-(*p*-dimethylaminophenyl)-silanol was treated with aniline, starting materials were recovered, and when di-*n*-butylamine was used, tris-(*p*-dimethylaminophenyl)-di-*n*-butylaminosilane was produced.[9] Attempts to prepare hexakis-(*p*-dimethylaminophenyl)-disiloxane by reaction between hexachlorodisiloxane and *p*-dimethylaminophenyllithium, or between tris-(*p*-dimethylaminophenyl)-chlorosilane and the sodium salt of tris-(*p*-dimethylaminophenyl)-silanol, yielded unidentified solids which decomposed without melting at temperatures above 400°.

Experimental

Triphenyl-(*p*-dimethylaminophenyl)-silane.—Triphenylchlorosilane was prepared by adding phenyllithium (0.45 mole) in ether to an ether solution of silicon tetrachloride (0.15 mole). To this solution *p*-dimethylaminophenyllithium[10] (0.10 mole) was added slowly, in a nitrogen atmosphere. The reaction mixture was hydrolyzed on completion of the addition, and the ether layer was dried and concentrated. The solid product which separated (46%) was recrystallized from petroleum ether (b.p. 60–90°) to give material melting at 144–146°. Some tetraphenylsilane (10%, m.p. 233–235°) was obtained as a by-product.

Treatment of an ether solution of the compound with ethereal hydrogen chloride gave triphenyl-(*p*-dimethylaminophenyl)-silane hydrochloride, which, after crystallization from absolute ethanol, melted at 227–229°.

Anal. Calcd. for $C_{26}H_{26}NClSi$: N, 3.37. Found: N, 3.00.

Diphenyl-bis-(*p*-dimethylaminophenyl)-silane was prepared in a similar fashion by adding two equivalents of phenyllithium and then two equivalents of *p*-dimethylaminophenyllithium to one equivalent of ethyl orthosilicate in ether. **Phenyl-tris-(*p*-dimethylaminophenyl)-silane** was made from ethyl orthosilicate by adding three equivalents of *p*-dimethylaminophenyllithium, followed by one equiva-

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(1) Gilman and Dunn, THIS JOURNAL, **72**, 2178 (1950).

(2) Gilman and Clark, *ibid.*, **68**, 1675 (1946).

(3) *Cf.* Gilman and Smart, *J. Org. Chem.*, **15**, 720 (1950).

(4) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(5) Cusa and Kipping, *J. Chem. Soc.*, 1040 (1933).

(6) Finholt, Bond, Wilzbach and Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

(7) Gilman, Melvin and Miller, unpublished results.

(8) Gilman and Marshall, THIS JOURNAL, **71**, 2066 (1949); Kipping and Cusa, *J. Chem. Soc.*, 1088 (1935); Kipping and Blackburn, *ibid.*, 1085 (1935).

(9) Gilman, Hofferth, Melvin and Dunn, *ibid.*, **72**, 5767 (1950).

(10) Gilman, Zoellner and Selby, *ibid.*, **55**, 1252 (1933).

TABLE I

PHENYL-*p*-DIMETHYLAMINOPHENYL SILANES

Silane	Yield, %	M.p., °C.	Empirical formula	Analyses, %			
				Calcd.		Found	
				N	Si	N	Si
Triphenyl-*p*-dimethylaminophenyl-	46	144–146	$C_{26}H_{25}NSi$	3.69	7.38	3.79	7.46
Diphenyl-bis-(*p*-dimethylaminophenyl)-	40	180–181	$C_{28}H_{30}N_2Si$	6.63	6.64	6.90	6.10
Phenyl-tris-(*p*-dimethylaminophenyl)-	17	171–173	$C_{30}H_{35}N_3Si$	9.03	6.02	9.30	6.29
Tetrakis-(*p*-dimethylaminophenyl)-	41	234–235	$C_{32}H_{40}N_4Si$	11.02	5.51	11.20	5.44

lent of phenyllithium. **Tetrakis-(*p*-dimethylaminophenyl)-silane** was prepared from one equivalent of silicon tetrachloride and four equivalents of *p*-dimethylaminophenyllithium. Yields, constants and analyses for these compounds are given in Table I. In all these preparations, reaction mixtures were hydrolyzed as soon as addition of the reagents was complete and while Color Test I[4] was still positive. The yields given in Table I were obtained under these conditions. It was found, however, that if a mixture of one equivalent of silicon tetrachloride and four equivalents of *p*-dimethylaminophenyllithium was refluxed in ether until Color Test I became negative (60 hours), yields of tetrakis-(*p*-dimethylaminophenyl)-silane as high as 86% could be obtained.

Bis-(*p*-dimethylaminophenyl)-silanediol.—*p*-Dimethylaminophenyllithium (0.17 mole) was added under nitrogen to 9.52 g. of silicon tetrachloride (0.056 mole) in ether. The addition was made over a 2-hour period while keeping the temperature of the reaction mixture at −15 to −20°. The solution was stirred for 30 minutes at room temperature, and then hydrolyzed. The ether layer was dried and distilled, leaving a sticky, blue solid which, after crystallization from benzene–petroleum ether (b.p. 90–120°) yielded 13 g. (77%) of bis-(*p*-dimethylaminophenyl)-silanediol melting at 173–174°.

Anal. Calcd. for $C_{16}H_{22}O_2N_2Si$: N, 9.27; Si, 9.27; active H, 2.0. Found: N, 9.43; Si, 9.10; active H, 1.93.

This compound was also synthesized by a second method. Bis-(*p*-dimethylaminophenyl)-diethoxysilane was prepared from ethyl orthosilicate and the aryllithium compound,[3] and 2 g. (0.005 mole) was dissolved in an excess of 0.1 *N* hydrochloric acid at room temperature. The immediate addition of dilute sodium hydroxide caused the precipitation of the silanediol. Recrystallization from benzene gave 1 g. (63%) of product melting at 172–173°. A mixed melting point with the material synthesized from silicon tetrachloride was not depressed.

Tris-(*p*-dimethylaminophenyl)-silanol.—*p*-Dimethylaminophenyllithium (0.18 mole) was added to 10.2 g. (0.06 mole) of silicon tetrachloride in ether under an atmosphere of nitrogen. During the addition of the first equivalent of aryllithium the temperature was kept at −15 to −20°, and while the last two equivalents were added dropwise the mixture was allowed to warm up to room temperature. It was then refluxed until Color Test I became negative (48 hours), and hydrolyzed. A solid insoluble in both ether and water was filtered off and dried. It weighed 2.5 g., melted at 224–228°, and was shown by mixed melting point to be tetrakis-(*p*-dimethylaminophenyl)-silane (8%). The ether layer on concentration deposited a brown, gummy solid which, when crystallized from benzene, gave 14 g. (58%) of colorless solid melting at 174–176°. Recrystallization from benzene raised the melting point to 183–184°. This compound has previously been reported as boiling at[11] 275–280° (12 mm.).

Anal. Calcd. for $C_{24}H_{31}ON_3Si$: N, 10.37; Si, 6.91; active H, 1.0. Found: N, 10.5; Si, 6.73; active H, 1.2, 0.9.

Tris-(*p*-dimethylaminophenyl)-chlorosilane.—This compound was prepared by the method used for tris-(*p*-dimethylaminophenyl)-silanol, except that, as soon as Color Test I became negative, the mixture was not hydrolyzed, but the ether was distilled off while adding dry benzene. When all the ether had been removed, the benzene solution was siphoned away from the inorganic salts under nitrogen, and concentrated. The yield of tris-(*p*-dimethylaminophenyl)-chlorosilane which crystallized out was 25.5 g. (60%), melting at 203–207°. Recrystallization from benzene gave 18.2 g. (43%), melting at 212–213°.

Anal. Calcd. for $C_{24}H_{30}N_3ClSi$: Cl, 8.38; Si, 6.61. Found: Cl, 8.20; Si, 6.93.

Tris-(*p*-dimethylaminophenyl)-ethoxysilane.—*p*-Dimethylaminophenyllithium (0.12 mole) was added in the usual way to 8.3 g. (0.04 mole) of ethyl orthosilicate in ether. After refluxing for 36 hours Color Test I was negative, and the mixture was hydrolyzed with water. Evaporation of the ether layer and crystallization of the product from ethanol–benzene gave 2 g. (11.5%) of material melting at 125–126°. Isolation of the reaction product from a similar run without the addition of water gave a 12% yield of the same material.

Anal. Calcd. for $C_{26}H_{35}ON_3Si$: N, 9.69; Si, 6.46. Found: N, 9.44; Si, 6.33.

This material was hydrolyzed by dissolving 7 g. (0.016 mole) of it in two equivalents of dilute hydrochloric acid and precipitating with 0.2 *N* sodium hydroxide. Recrystallization from absolute ethanol gave 5.7 g. (80%) of tris-(*p*-dimethylaminophenyl)-silanol, m.p. 184–185°. This did not depress the melting point of the material obtained from silicon tetrachloride.

Diphenyl-(*p*-dimethylaminophenyl)-silanol.—*p*-Dimethylaminophenyllithium (0.06 mole) was added slowly to a refluxing solution of 15.2 g. of diphenyldichlorosilane (0.06 mole) in ether. The solution was refluxed for a total of 2 hours, then hydrolyzed. An ether-insoluble layer separated and was extracted with chloroform. This chloroform, on concentration, deposited 4.8 g. of diphenylsilanediol. On evaporation of the dried ether layer a residue remained which was extracted with benzene. A benzene-insoluble residue consisted of 1.6 g. of diphenylsilanediol, making the total yield of this material 6.4 g. or 49%. The benzene solution, on concentration, left an oil which solidified on cooling and after several crystallizations from benzene–petroleum ether (b.p. 90–120°) weighed 4 g. and melted at 65–66°. This proved to be diphenyl-*p*-dimethylaminophenylsilanol; yield 21%.

Anal. Calcd. for $C_{20}H_{21}ONSi$: Si, 8.79; active H, 1.0. Found: Si, 8.98; active H, 0.96.

Tris-(*p*-dimethylaminophenyl)-silane.—*p*-Dimethylaminophenyllithium (0.11 mole) was added to 4.97 g. (0.037 mole) of silicochloroform in ether. The first equivalent of aryllithium was added at −10°, but during the remainder of the addition the mixture was allowed to warm up to room temperature. Color Test I did not become negative until the reaction mixture had been refluxed for 30 hours. Dilute ammonium chloride solution was then added and the ether layer separated. On concentration of the ether solution there was obtained 7 g. (49%) of solid melting at 153–155°. Recrystallization from absolute ethanol raised the melting point to 157°.

Anal. Calcd. for $C_{24}H_{31}N_3Si$: N, 10.79; Si, 7.19; mol. wt., 389. Found: N, 10.6; Si, 6.92; mol. wt. (cryoscopic in benzene), 387 ± 7.

This compound did not evolve hydrogen when treated with potassium hydroxide in piperidine as do most triarylsilanes,[5] but when 1 g. (0.0026 mole) of the material was warmed to 60° with 50 ml. of 2% potassium hydroxide in absolute ethanol a vigorous evolution of gas took place and the triarylsilane dissolved. When reaction was complete an equal volume of benzene was added and the mixture was made just acid to phenolphthalein with 0.1 *N* hydrochloric acid. The benzene solution was washed free of alcohol and inorganic materials and dried. Evaporation of the benzene and crystallization of the residue from benzene–petroleum ether (b.p. 90–120°) yielded 1 g. (85%) of material melting at 177–178° which was identified as tris-(*p*-dimethylaminophenyl)-silanol by mixed melting point.

Tris-(*p*-dimethylaminophenyl)-silane was also prepared by refluxing 1 g. (0.0024 mole) of tris-(*p*-dimethylamino-

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[11] Fleming, U. S. Patent 2,386,452 (1945) [*C. A.*, **40**, 603 (1946)].

phenyl)-chlorosilane with 0.1 g. (0.0027 mole) of lithium aluminum hydride in ether for 6 hours. The mixture was hydrolyzed by adding ether saturated with water, and the aluminum hydroxide was washed out with dilute aqueous acetic acid. The dried ether solution, on standing, deposited 0.9 g. (98%) of tris-(*p*-dimethylaminophenyl)-silane, m.p. 157°, without recrystallization. This was identified by a mixed melting point determination with the sample reported above.

Attempted Preparation of Hexakis-(*p*-dimethylaminophenyl)-disiloxane.—All attempts to prepare this compound from tris-(*p*-dimethylaminophenyl)-silanol were unsuccessful. Refluxing the silanol with glacial acetic acid,[7] 98% formic acid[7] or hydrochloric acid in methanol[12] gave glasses or oils with a strong blue color which suggests that cleavage of the *p*-dimethylaminophenyl group had taken place.[8]

One gram of tris-(*p*-dimethylaminophenyl)-silanol (0.0025 mole) was suspended in dry xylene and 0.5 g. (0.022 g. atom) of sodium metal was added. This was warmed until the silanol had completely dissolved and hydrogen was no longer evolved. The solution was then decanted into a xylene solution of 1 g. (0.0024 mole) of tris-(*p*-dimethylaminophenyl)-chlorosilane. This mixture was refluxed for 6 hours, then washed with water, and 0.4 g. of colorless insoluble material was filtered off. This solid did not melt, but slowly turned brown and decomposed when heated above 400°. A product with very similar properties was obtained when 5.22 g. (0.0183 mole) of hexachlorodisiloxane was refluxed in ether with 0.11 mole of *p*-dimethylaminophenyllithium until Color Test I became negative (15 hours). Purification of the crude product was attempted by dissolving it in dilute acid, washing the solution with ether, and reprecipitating with dilute aqueous ammonia. The material so obtained had a satisfactory silicon analysis for hexakis-(*p*-dimethylaminophenyl)-disiloxane (calcd. 7.07, found 6.96) but its cryoscopic molecular weight in nitrobenzene was much too low (calcd. 792, found 440 ± 30). In view of these anomalous results, we do not claim that this material is hexakis-(*p*-dimethylaminophenyl)-disiloxane.

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[12] Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS DIVISION, UNION CARBIDE AND CARBON CORPORATION]

Some Thermodynamic Properties of Hexadecafluoroheptane[1]

BY GEORGE D. OLIVER AND J. W. GRISARD

The heat capacity of hexadecafluoroheptane was measured over the temperature range of 18 to 310°K. A transition that absorbed 1594 ± 1.5 cal./mole was found at 180.46 ± 0.10°K. The triple point, 221.87 ± 0.05°K., and heat of fusion, 1660.5 ± 2 cal./mole were determined. Vapor pressure measurements were made for the temperature range −2 to 106° and are represented by the equation $\log_{10} P_{\text{mm.}} = 6.96493 - 1196.067/(t + 210.36)$. The calculated heat of vaporization is 7543 cal./mole at a boiling point of 82.50 ± 0.05°. The critical constants are: t_c, 201.7°, p_c, 16.0 atm. and d_c, 0.584 g./ml. Entropy values calculated from these data for the liquid and ideal gas state at 298.16°K. are 134.28 ± 0.27 and 158.88 cal./deg. mole, respectively.

Introduction

Very little work has been done on the thermodynamics of pure fluorocarbons, probably due to the difficulty of obtaining pure samples. Since fluorocarbons are becoming increasingly important in industrial and academic laboratories, it is desirable to obtain precise data which can be applied to practical as well as fundamental problems. Therefore, the vapor pressure and low temperature thermal properties of hexadecafluoroheptane have been measured and other properties have been calculated from the data.

Experimental

Materials.—The samples were part of a lot of technical grade material produced by the fluorination of *n*-heptane with cobalt trifluoride.[2] Most of the impurities were removed by fractional crystallization, while further purification was obtained by passing the best of this crystallized material through a 56-foot silica gel adsorption column.[3] An estimate of the mole per cent. impurity in the purer sample as determined from melting point studies in this research is given in Table I. A different sample was used for vapor pressure measurements. Its purity was approximately 99.92 mole per cent. as deduced from time–temperature freezing curves.

TABLE I

MELTING POINT SUMMARY

0°C. = 273.16°K.

Melted, %	21.9	39.8	44.9	72.1	84.7
$T_{\text{obsd.}}$, °K.	221.730	221.789	221.794	221.822	221.830

Triple point, 221.87 ± 0.05°K. $N_x = 0.0168\,\Delta T$. Impurity = 0.06 ± 0.02 mole per cent.

Apparatus.—The calorimetric apparatus was similar to that described by Ruehrwein and Huffman,[4] who improved the design of Blue and Hicks,[5] mainly, by the addition of the vacuum windlass and by the use of alternating current in the shield heater circuits. Two modifications were made which should be mentioned[6]: The heater, made of size No. 36 Advance wire, was bifilarly wound on a copper sleeve which enveloped a 25.5 ohm commercial platinum resistance thermometer. The copper sleeve, greased with Apiezon N, fitted tightly in a well in the calorimeter and in turn the greased thermometer fitted tightly inside the heater. The other modification consisted of a separate differential couple between the shield and ring which indicated their temperature difference on an additional galvanometer and scale.

A brief description of the apparatus and procedure follows: Approximately 50 ml. of the material was sealed in a copper calorimeter and mounted in the adiabatic calorimetric system. To prevent heat interchange, the temperature of the environment was maintained at that of the calorimeter by means of an electrically heated shield as indicated by differential thermocouples. All electrical measurements needed to determine the temperature and energy involved were made on a White double-potentiometer in conjunction with a high sensitivity galvanometer and calibrated resistances. An Eppley cell certified by National Bureau of Standards was used as a potential reference. Time measurements were made with an electric stop-clock which was frequently

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[1] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

[2] R. G. Benner, *et al.*, *Ind. Eng. Chem.*, **39**, 329 (1947).

[3] S. Blumkin, N. C. Orrick, J. W. Grisard and J. D. Gibson, "Purification of Hexadecafluoroheptane," to be published at a later date.

[4] R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943).

[5] R. W. Blue and J. F. G. Hicks, *ibid.*, **59**, 1962 (1937).

[6] G. D. Oliver, J. W. Grisard and V. E. Anderson, Instrumentation, K-550, Carbide and Carbon Chemicals Division, K-25 Plant, Oak Ridge, Tennessee, January 20, 1950. Detailed description and drawings of the apparatus are presented.