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SOME CORRELATIONS BETWEEN STRUCTURE AND THERMAL STABILITY OF ORGANOSILICON COMPOUNDS

by

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INTRODUCTION

The study of the chemistry of organosilicon compounds has received a tremendous impetus in recent years with the discovery of interesting and useful properties quite different from those of related carbon analogs. Of these properties, the great thermal stability of many of these silicon compounds has been exploited very successfully. There exist, however, only the most preliminary investigations to establish the theoretical grounds for this resistance to high temperatures. There is no published systematic study to determine qualitatively the susceptibility to thermal decomposition of various organic moieties bonded directly to the silicon atom.

This work was undertaken in the hope of synthesizing organosilicon compounds for possible use as synthetic lubricants at very high temperatures. The synthesis excluded all materials containing the silicon-oxygen bond. Because of the empirical approach required by lack of previous or published studies, there will appear in the Experimental part some rather non-systematic and unrelated individual compounds. If the organic group chosen did not seem to impart thermal resistance to a molecule, no further work was done with it. Promising groups were incorporated in a defined series of compounds to obtain more complete data and investigate any possible trends and deviations. A table listing the data obtained from thermal stability tests carried out on the synthesized compounds follows the Experimental part.

In the Historical part, the literature concerned with the relative stabilities of organosilicon compounds has been thoroughly reviewed through 1953 and as well as possible into May 1955[1]. Publications dealing with compounds containing the silicon-oxygen-carbon linkage are also included.

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[1] Chemical Abstracts were reviewed through the 1953 index. The Journal of the American Chemical Society, the Journal of Organic Chemistry and Current Chemical Papers have been covered through May, 1955. Chemical Reviews were checked through April, 1955.

HISTORICAL

Much has been written[2,3,4,5,6] describing the preparation, properties and uses of organosilicon compounds. However, the literature is very sparse on the subject of the theoretical basis for the high thermal stability of some of these compounds.

It would be of advantage to qualify here what is meant by the term thermal stability. In the context of this study it will mean the cleavage of one or more of the organosilicon bonds. Considering this criterion, the data most vital to the discussion will be that of the energy required to rupture these bonds. A measure of this energy is often described as the bond dissociation energy.

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[2] C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, Chem. Revs., 41, 97 (1947).

[3] H. W. Post, "Silicones and Other Organosilicon Compounds", Reinhold Publishing Corp., New York, N. Y., 1949.

[4] E. G. Rochow, "An Introduction to the Chemistry of the Silicones", 2nd ed., John Wiley & Sons, New York, N. Y., 1951.

[5] H. Gilman and G. E. Dunn, Chem. Revs., 52, 77 (1953).

[6] P. R. McGregor, "Silicones and Their Uses", McGraw-Hill Book Co., Inc., New York, N. Y., 1954.

Pyrolytic decomposition is generally considered[7,8] to be due to the accumulation of amplitudes of thermal vibration of one bond. It is also stated that the order of cleavage of organic groups in this decomposition varies with the experimental conditions. The variation in individual stability is explained by assuming two antagonistic factors. The first, tending to favor stability, is a steric factor which depends on the increasing number and structural organization of the carbon atoms. The second, tending to decrease stability, is a polar factor. There is also noted that the higher stability of aromatic molecules, compared to paraffins of similar molecular weight, may be due to the fact that cleavage of one aromatic bond does not result in the decomposition of the entire molecule as would be the case for the paraffin.

From these statements it can be assumed that, in general, the aryl organometallic compounds are more thermally resistant than the corresponding alkyl compounds of like molecular weight. Also, that for alkyl-metallic compounds, stability increases with increasing chain length. From the

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[7] I. V. Obreimov, Zhur. Eksptl. Teoret. Fiz., 19, 396 (1949). [Original not available for examination; abstracted in C. A., 46, 9906 (1952).]

[8] G. Petit, Bull. soc. chim. France, 10, 224 (1943) [C. A., 39, 271 (1945)].

generalizations in the literature, the aryl compounds are the more stable, but, the smaller chain alkyl-metallic molecules decompose less readily than do their longer chain homologs.

In the organosilicon compounds more work has been done on molecules containing the silicon-oxygen-carbon bond than on aryl- and alkyl-substituted silanes. Dolgov and Volnov[9], testing the theory of Hertkorn[10], that an oxygen atom between the carbon and silicon atoms weakens the attractive forces between the latter two, have found the following results. The work was done in a hydrogen atmosphere. Tetraethoxysilane, heated for 25 hours at 200° and 100 atmospheres, gave ethanol and hexaethoxydisilane as products. At 280° the same ethoxy compound was decomposed into ethylene and tetrahydroxysilane. (Tetraethylsilane is stable under comparable conditions.) Tetraphenoxysilane was completely cleaved at 380° into phenol and silicon. The corresponding tetra-*p*-cresoxysilane afforded silicon dioxide as well as silicon and *p*-cresol. Tetrahexyloxysilane gave quantitative yields of hexyne and silicon dioxide.

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[9] B. N. Dolgov and Yu. N. Volnov, *J. Gen. Chem.* (*U. S. S. R.*), *1*, 330 (1931) [*C. A.*, *26*, 2168 (1932)].

[10] J. Hertkorn, *Ber.*, *18*, 1697 (1885).

In the case of ester chlorides of orthosilicic acid, it can be stated[11] that stability increased with increase in molecular weight. The aromatic esters resisted thermal decomposition more readily than the aliphatic esters. There was also a notable decrease in stability from the normal to iso esters. It may be of interest to note here that such compounds as triethoxychlorosilane, hexyloxytrichlorosilane and o-anisyltrichlorosilane gave silicon tetrachloride as one of the decomposition products.

Gilman and Dunn[5], in their comparison of analogous compounds of carbon and silicon, have found that even though the bond dissociation energy of the carbon-carbon bond is greater than that of the silicon-carbon bond, some compounds containing the latter linkage are very stable at high temperatures. Tetraphenylsilane can be boiled without decomposition at temperatures as high as 428°, and is stable to 500° and higher. Tetraphenylmethane resists these conditions equally well. There is, however, the expected finding that the tetraalkyl silanes are more susceptible to thermal cleavages than their carbon analogs.

The same authors claim that the weakness of the silicon-silicon bond is a factor in the paucity of molecules containing

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[11] Yu. N. Volnov, J. Gen. Chem. (U. S. S. R.), 17, 1428 (1947) [C. A., 42, 2230 (1948)].

such a bond. However, they further state that the thermal instability of this type of linkage is most probably not the entire reason for the scarcity of these compounds. Examples of this type, such as 1,2-diethyl-1,2-diphenyl-1,2-dipropyldisilane and hexaphenyldisilane which have a boiling point of 268° at 100 mm. and melting point of 355° respectively, resist all decomposition at these temperatures.

There appears to be a case in which the silicon-silicon bond is stronger than the corresponding carbon-carbon analog. Hexaphenyldisilane, prepared by Schlenk to compare its tendency with that of hexaphenylethane to dissociate into free radicals, is more stable than the bond energies would predict. In fact, two other such compounds, hexa-p-tolyldisilane and hexa-p-biphenylyldisilane, melt undecomposed at temperatures above 350°. The authors point out two factors in the disilanes important in an explanation of the unexpected stability. The first is that the steric strains in this type of compound should be considerably smaller than in analogous carbon compounds because of the larger size of the silicon atoms. The second is a decreased resonance stabilization due to the very low ability of silicon to form silicon-carbon double bonds.

In a recent study[12] on chlorinated chloromethylsilanes and methylsiloxanes, Zimmermann discovered a series of extremely labile organosilicon compounds. He postulates the following structural requirements for these molecules which decompose almost explosively. There must be present the trichloromethyl group; at least one hydrogen bonded to a carbon atom; and the latter carbon atom directly connected to the silicon atom. The compound, trichloromethyldimethylchlorosilane, falls into this group. The compound, trichloromethyltrichlorosilane, was found to be quite stable. He also noted that lesser chlorinated molecules, present as impurities, tend to stabilize the labile compounds. This he ascribed to the formation, through intermolecular reactions, of materials structurally different from those defined in the above criteria. It is possible to cause a slow and continuous decomposition of the explosive types by gentle heating, avoiding any localized overheating. The cleavage products obtained almost always include hydrogen chloride and different silicon-chlorine bonded molecules. Examples of the variety of cleavage products from trichloromethyldimethylchlorosilane are hydrogen chloride, chloroform,

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[12] W. Zimmermann, Ber., 87, 887 (1954).

hexachlorobenzene, methyltrichlorosilane and silicon mixed with carbon. It is of interest to note that the carbon analog, 1,1,1,2-tetrachloro-3-methyl propane, is quite stable at the conditions required to decompose the corresponding silane.

Fritz[13] has isolated from the thermal decomposition of silane, a small quantity of disilane. The monosilane was heated to 470-480° at 4 mm. and then quickly cooled. It was his intention to show that the above decomposition did take place through a free radical mechanism. Earlier workers[14], unable to isolate any disilane, proposed a non-radical type mechanism. This author claims that the temperatures previously employed were high enough to quickly decompose any disilane formed.

The same author[15] has carried out some experiments on the decomposition of ethylsilanes such as ethylsilane, diethylsilane and triethylsilane. At 480°, diethylsilane gave the following products: ethylene, silane, methylsilane, dimethylsilane, propane, propene, $C_9H_{24}Si_2$, a high boiling

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[13] G. Fritz, Z. Naturforsch., 7B, 507 (1952).

[14] T. R. Hogness, T. L. Wilson and W. C. Johnson, J. Am. Chem. Soc., 58, 108 (1936); H. J. Emeleus and C. Reid, J. Chem. Soc., 1939, 1021.

[15] G. Fritz, Z. anorg. u. allgem. Chem., 273, 275 (1953).

oil, and a solid of empirical formula $(CH_3Si)_x$. The C_9-compound was found to be monomeric in benzene and to contain the silicon-silicon bond. It was not further identified. Pyrolysis of ethylsilane and triethylsilane also gave tetramethylsilane in addition to products similar to those mentioned.

The patent literature[16] describes the preparation of some vinyl-aromatic silanes by the pyrolysis of a beta-chlorinated organosilicon compound of general formula $X_3Si-A(Y)RBSiX_3$, where A is a saturated tervalent carbon radical; B is a saturated bivalent carbon radical; R is a bivalent aromatic radical; and X and Y are halogens. Materials of this type are obtained from molecules prepared by the reaction of a haloalkylsilane, such as 1- or 2-chloroethyltrichlorosilane, and an aromatic compound, such as benzene, in the ratio of 2:1 in the presence of aluminum chloride. The latter reagent is removed from the reaction mixture as an aluminum chloride-phosphorus(V)oxychloride complex. Chlorination of the products, such as bis-(beta-trichlorosilylethyl)-benzene, from this reaction yields materials having the structural requirements listed above.

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[16] D. B. Hatcher and R. H. Bunnell, U. S. 2,570,551 (Oct. 9, 1951). [Original not available for examination; abstracted in C. A., 46, 4568 (1952).]

They are then pyrolyzed at 300-400° in the presence of an inert gas. In an example, the products of the chlorination of bis-(beta-trichlorosilylethyl)-benzene, when pyrolyzed, gave silicon tetrachloride, divinylbenzene and a fraction boiling in the range 150-210° at 3 mm. Redistillation of the latter material gives the desired vinyl-beta-trichlorosilylethylbenzene. It is of interest to note the results[17] of some qualitative studies on the stability of certain organic groups carried out by a number of workers in This Laboratory[18]. The basic structure of the molecules consisted of phenyl groups attached to silicon or other Group IVB elements. The organic moieties other than phenyl were then considered to be the cause for variations in susceptibility to thermal cleavage.

One group of compounds which showed promise contained long-chained, n-alkyl substituents. Tetra-n-undecyl-,-n-dodecyl-,-n-tetradecyl-,-n-hexadecyl- and -n-octadecylsilane all volatilized, at regularly increasing temperatures between

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[17] The compounds, contained in a capillary melting point tube, were placed in an electrically-heated, copper block and observed through a mica window cut into the base of the block. Volatility was determined by the presence of a liquid in that part of the tube extending above the copper.

[18] C. W. Gerow, J. J. Goodman, R. D. Gorsich, R. K. Ingham, D. H. Miles and K. Oita, unpublished studies, Iowa State College.

435-460°, without any signs of decomposition. All but the latter two are liquids at room temperature. When phenyl groups were introduced into the molecules there were signs of a decrease in stability as indicated by a yellow coloration of the compounds near their boiling points. Triphenyl-n-decyl-, -n-dodecyl-, and -n-octadecylsilane were pale yellow liquids at 400° and volatilized at about 442-445°. The bis-substituted compounds, such as diphenyl-bis-(n-dodecyl)-silane, were found to boil in an intermediate range. The general trend does indicate that the more n-alkyl groups of the length C_{11}-C_{18}, the higher the volatilization temperatures. The shorter-chained molecules vaporized at somewhat lower temperatures, yet, there were no signs of decomposition. Triphenylmethylsilane was volatilized at 300° without any previous discoloration or residue. Triphenyl-n-propyl-, -n-butyl-, and -n-hexylsilane have boiling points at about 365°, 380° and 400°, respectively.

Another series tested was of the mixed alkyl-aryl types. The compounds triphenylbenzyl-, diphenyldibenzyl- and phenyltribenzylsilane volatilized well above 400°. The tribenzyl-substituted molecule volatilized about 15° higher than the other two mentioned. None of the three showed signs of decomposition. Materials having the aromatic group further out on the chain, triphenyl-beta-phenylethylsilane and diphenyl-bis-(gamma-phenylpropyl)-silane, are somewhat more susceptible to decomposition.

Polycyclic groups gave a variety of results. A series of phenyl-9-fluorenyl-silanes tested showed that an increase in the number of 9-fluorenyl groups raised the vaporization temperature considerably. However, all these molecules gave a deep red color at about 400°. Tests on some 1-indenyl-containing compounds showed no definite trends. Triphenyl-1-indenylsilane, melting point 136°, became slightly milky at 400° and volatilized at about 430° without any residue. However, 1,1-bis-(triphenylsilyl)-indene, melting point 206°, was light yellow at 400°; light brown by 423°; red-brown by 450° and black at 465°. The residue finally volatilized at 470°. Another group of considerable interest was the 2-biphenylyl. The members of this series had vaporization temperatures between 480-520°. In all cases there was considerable darkening of the liquid melt and a colored residue at the vaporization points. Both the alpha- and beta-naphthyl groups were tested and showed greater thermal resistance than the phenyl groups. Triphenyl-alpha-naphthylsilane volatilized from 472-474° without visible decomposition. the beta isomer became a light-yellow liquid at that temperature and finally vaporized at about 490°. The number of available molecules containing these groups was so small that a generalization or trend in thermal stability properties was not possible.

Another series tested contained halogen-substituted phenyl groups. The variations included not only the type of halogen but also its position on the ring. From these studies it was concluded that the disposition of the halogen on the benzene ring does not materially affect thermal stability. There was, however, a noticeable difference in boiling temperature between the chlorophenyl and fluorophenyl groups tested. Tetrakis-(m-fluorophenyl)-silane volatilized at 394°; the chlorine analog at 472°. Neither showed appreciable decomposition. The melting points of the fluorine-substituted phenyl groups were generally much higher than those for corresponding chlorine compounds. The bromine and iodine analogs were not available for study.

Molecules containing a silicon-oxygen bond showed varying thermal properties. Hexaaryldisiloxanes of the type $(Ar_3Si)_2O$ were found to be quite stable to decomposition. Mixed alkyl-aryl disiloxanes, such as 1,1,1-trimethyl-3,3,3-triphenyldisiloxane, were vaporized in the range 340-370°. A fully alkylated disiloxane, hexa-n-butyldisiloxane, was volatilized at about 325°. All members of this class of compounds showed little signs of decomposition at their boiling points. Of the silanols tested, triphenyl- and tribenzylsilanol were converted to the corresponding hexasubstituted disiloxanes on heating well above their boiling points. The boiling ranges for those molecules which retained their chemical structures extended from about 292° for diphenyldiethoxysilane to 450° for triphenylbenzhydryloxysilane. There was a much more consistent trend noted in resistance to decomposition by this class of compounds. With the exception of several members which became slightly yellow, the representatives of this class were vaporized without decomposition.

In the heterocyclic series several compounds containing the dibenzothiophene system were screened. The 3-trimethylsilyldibenzothiophene volatilized at about 362-364° without signs of decomposition. The analogous 4-position isomer was black at 485° and left a residue on boiling at 535-540°. Since there was some doubt as to the purity of the latter sample, no generalizations could be made. The 2-, -3- and 4-trimethylsilyldibenzothiophene-5-dioxide were also tested. All three volatilized at temperatures of 420-427° without extensive decomposition. The latter, however, was a pale-yellow color near its boiling point. In this case again, the paucity of molecules for observation makes any sound generalization difficult.

A very definite conclusion can be drawn from the tests conducted on analogous compounds differing only in the Group IVB element present. One series studied was the type containing four phenyl groups. It is interesting to note that the melting points of tetraphenylsilane,-germane, -tin, and -lead lie within the range 228-233°. However, the silane and germane boil undecomposed at temperatures of 428-430° and 433-435° respectively. Tetraphenyltin leaves a gray residue at 400°, and tetraphenyllead is decomposed into a black mass at 275°. Another similar series screened contained the triphenylbenzyl-group. Again all members had similar melting points, 88-92°. In this case the triphenylbenzylsilane vaporized at a temperature slightly above that of the germanium analog. The corresponding tin and lead compounds decomposed into black residues at much lower temperatures. From a considerable number of other individual specimens tested, it can be unequivocally stated that tin- and lead-containing materials are definitely more susceptible to thermal cleavages than those of silicon and germanium. A comparison of the organometallic compounds of silicon and germanium leads to no clear-cut classification at this time. Triphenylsilane and triphenylgermane, both melting at about 42-45°, volatilize undecomposed at 350° and 354° respectively. The corresponding tetrakis-_n_-

tetradecyl molecules are not nearly so similar. The silane becomes a vapor in the vicinity of 435-440° without decomposition. Tetrakis-n-tetradecylgermane, on the other hand, became light to dark brown through the range 372-411°, and generally volatilized at about 415° leaving a small amount of residue. In the case of hexaphenylgermoxane and hexaphenyldisiloxane, the melting points are 185° and 227-229° respectively; and the corresponding volatilization temperatures 480° and 515°. Thus, it can be seen that in some cases the silicon-containing molecule possesses greater thermal stability; in others, the organo-germanium compound is superior in this respect. From the evidence available at this time there seems to be a significant increase in thermal resistivity of fully-alkylated and triphenyl monoalkylated silanes when compared with their germanium analogs.

It is essential to point out here that the volatilization of the screened molecules does not necessarily coincide with any decomposition temperatures. On the contrary, those materials noted to have vaporized without decomposition were probably capable of withstanding a great deal more heat before any bond cleavage would take place. The rather qualitative measuring technique employed was primarily intended to give an order of magnitude of stability from room temperature to the vaporization point.

Gilman and Bailie[19] have carried out a study on the pyrolysis of some organolead compounds of the type R_3PbPbR_3. Perhaps the data given on the ease of cleavage of various organic moieties may be of a general nature regardless of the Group IVB central atom. The materials were heated in xylene and the time required to deposit lead noted. The authors give the following order of decreasing thermal stability: mesityl, cyclohexyl, alpha-naphthyl, o-ethoxyphenyl, o-methoxyphenyl, o-tolyl, p-ethoxyphenyl, p-methoxyphenyl, p-tolyl, m-tolyl, phenyl, ethyl and methyl. The first three members of the series showed no deposition of lead after 6 hours of refluxing in xylene. The authors ascribe this thermal resistance partially to steric factors. They also point out that all three lead compounds were prepared in rather low yields. Position isomers were noticeably different in their susceptibility to pyrolytic cleavage. The o-methoxyphenyl and p-methoxyphenyl molecules took 60 minutes and 3-5 minutes, respectively, to deposit metal. The corresponding ethoxy compounds gave black solids in 17 minutes and 1-3 minutes. In the tolyl series, the order ortho, meta and para took 45, 0 and 3-5 minutes, respectively, for deposition to be noted. These results do not agree with

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[19] H. Gilman and J. C. Bailie, J. Am. Chem. Soc., 61, 731 (1939).

the previously mentioned study in the silane series in which position isomers possessed no significant difference in thermal resistance. They do, however, give credence to the importance of steric factors in this problem. Hexaphenyldilead decomposed immediately in the boiling xylene. The alkyldilead molecules, such as hexaethyl- and hexamethyldilead, were cleaved before the boiling temperature of the xylene solution was attained. This result agrees well with the generalization that short-chained alkyl groups show very poor thermal stability.

EXPERIMENTAL

General Procedure[20]

Inert atmosphere

Nitrogen. Commercially available, prepurified (99.9% pure) nitrogen was used throughout the study.

Apparatus

The apparatus used for all experiments consisted of a 3-necked, round-bottomed flask, Tru-bore stirrer with glass paddle and reflux condenser. All of the equipment was dried in an oven at 100° and allowed to come to room temperature under nitrogen. This inert atmosphere was maintained throughout the entire experiment if an organometallic reagent was an intermediate in any of the reactions.

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[20] All melting points reported here are uncorrected values. They were determined by the capillary tube method at a rate of heating of 1°/minute near the melting point. An electrically-heated, copper block was used throughout the entire study.

Reagents

Solvents. The diethyl ether was a commercial, anhydrous grade stored over sodium wire. All other solvents employed were commercially available "reagent grades". They were stored over sodium wire for at least 24 hours prior to use.

Organic halides. The organic halides employed for the preparation of the corresponding organolithium or Grignard reagents were of Eastman "white label" or equivalent grade of purity. They were not further purified before use.

Lithium. The lithium wire was one-eighth of an inch in diameter and weighed 3.4 to 3.7 g. per meter. The wire, coated with grease, was stored under mineral oil. The protective coatings were carefully wiped off with a towel before the wire was cut into small pieces. Excess metal, if present after the completion of a reaction was removed by filtration of the organolithium solution through loosely-plugged glass wool.

Magnesium. The commercially available grade labeled "for Grignard reaction" was used for all preparations. Unreacted magnesium was separated from the reaction mixture by the method used for the removal of excess lithium.

Product isolation procedure

After completion of the reaction period, the resultant mixture was hydrolyzed. Water was the reagent normally employed for organolithium preparations. In the experiments using Grignard reagents, the hydrolysis was carried out with 3 N hydrochloric acid. The organic layer was separated and dried over anhydrous sodium sulfate for at least 4 hours. The solvent was then distilled at atmospheric pressure. Treatment of the residue is described under the individual compounds.

Alkyllithium Compounds

n-Butyllithium

The procedure used was in essential accordance with that reported by Gilman and co-workers[21]. The modification employed was cooling the reaction mixture to a temperature between -35 and -40° after the addition of the *n*-butyl bromide-ether solution had been started. A representative preparation follows.

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[21] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *J. Am. Chem. Soc.*, *71*, 1499 (1949).

To a stirred suspension of 4.56 g. (0.66 g. atom) of lithium wire (cut into pieces less than 1 cm. in length) in 150 ml. of ether were added 30 drops of a solution containing 41.1 g. (0.30 mole) of n-butyl bromide in 75 ml. of ether. As soon as the reaction began, as indicated by a turbidity in the stirred solution, the mixture was cooled to -35° by means of a Dry Ice-acetone bath. The dropwise addition of the remainder of the ethereal solution was begun. This addition required 30 minutes. The temperature of the reaction mixture was carefully maintained between -35 and -40° during this period by raising or lowering the bath. The mixture was stirred at this temperature for 30 minutes after completion of the addition. Then the bath was removed and the reaction mixture allowed to stir for 2 more hours at 0°. The yield of n-butyllithium as determined by the double titration method[22] was 89%.

In succeeding preparations the yields ranged from 86-92%.

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[22] H. Gilman and A. H. Haubein, ibid., 66, 1515 (1944).

Aryllithium Compounds

Phenyllithium

This reagent was prepared according to the procedure of Jones and Gilman[23]. A typical preparation follows.

To a stirred suspension of 3.10 g. (0.445 g. atom) of lithium wire (cut into pieces less than 1 cm. in length) in 150 ml. of ether were added 10 ml. of a solution of 33.0 g. (0.210 mole) of bromobenzene in 75 ml. of ether. The solution became turbid after several minutes. The remainder of the ethereal solution was then added at a rate sufficient to maintain gentle reflux of the reaction mixture. After the addition was completed, external heat was supplied to continue the refluxing for an additional 30 minutes. The yield, determined by a simple acid titration[24] was 97%.

In succeeding preparations the yields ranged from 94-100%.

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[23] R. G. Jones and H. Gilman in R. Adams, "Organic Reactions", John Wiley & Sons, Inc., New York, N. Y., 1951, Vol. 6, p. 354.

[24] H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, J. Am. Chem. Soc., 45, 150 (1923).

Organosilicon Compounds

1,4-Bis-(triphenylsilyl)-benzene

To 200 ml. of an ethereal solution containing 0.190 mole of n-butyllithium were slowly added 150 ml. of an ethereal solution containing 22.4 g. (0.095 mole) of p-dibromobenzene[25]. The temperature of the reaction mixture was maintained (by means of a Dry Ice-acetone bath) at -15° during addition. Color Test II[26] was found to be negative one hour after completion of the addition. To this mixture were then slowly added 250 ml. of an ethereal solution containing 56.0 g. (0.190 mole) of triphenylchlorosilane. A white precipitate formed during the addition. Color Test I[27] was negative on completion of the addition. The mixture was allowed to come to room temperature and stirred for one hour.

The solid was filtered off, washed with 200 ml. of water and dried. There was obtained 35.2 g. of white powder

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[25] H. Gilman and R. G. Jones, ibid., 63, 1443 (1941).

[26] H. Gilman and J. Swiss, ibid., 62, 1847 (1941).

[27] H. Gilman and F. Schulze, ibid., 47, 2002 (1925).

melting over the range 338-356°. The ether layer was hydrolyzed with 500 ml. of water. The organic layer was separated, dried and distilled. There remained a white solid melting over the range 344-358°. One recrystallization of the combined solids from tri-n-butyl phosphate gave only 23.7 g. (42.0%) of pure product melting sharply at 360°.

Anal.[28] Calcd. for $C_{42}H_{34}Si_2$: Si, 9.45. Found: Si, 9.41, 9.47.

Bis-(p-triphenylsilyl)-phenyl ether

To 180 ml. of an ethereal solution containing 0.165 mole of n-butyllithium (at -15°) were slowly added 125 ml. of an ethereal solution containing 27.1 g. (0.083 mole) of di-p-bromophenyl ether[29]. Color Test II was negative after 15 minutes. There were then added 300 ml. of an ethereal solution containing 48.6 g. (0.165 mole) triphenylchlorosilane. The blue color of the organometallic reagent was

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[28] Most silicon analyses were carried out according to the procedure of H. Gilman, B. Hofferth, H. W. Melvin, Jr. and G. E. Dunn, ibid., 72, 5767 (1950). For those compounds which have a silicon-containing group easily volatilized during this procedure, note will be made to reference 43 describing a modified analysis.

[29] H. Gilman, W. Langhorm and F. W. Moore, ibid., 62, 3277 (1940).

discharged on completion of addition. Color Test I was negative after 10 minutes. The reaction mixture was allowed to come to room temperature and then refluxed for 2 hours with constant stirring.

The cooled solution was then hydrolyzed with 300 ml. of water. The ether layer was separated, dried, and distilled. There was obtained 46.4 g. of a white solid melting over the range 289-306°. This material was recrystallized from tri-n-butyl phosphate. There was finally obtained 26.1 g. (45.2%) of white crystals melting at 306-307°.

Anal. Calcd. for $C_{48}H_{38}OSi_2$: Si, 8.19. Found: Si, 8.22, 8.25.

Diphenyl-bis-(p-phenoxyphenyl)-silane

To 105 ml. of an ethereal solution containing 0.090 mole of n-butyllithium were slowly added 75 ml. of an ethereal solution containing 22.4 g. (0.090 mole) of p-bromophenyl phenyl ether.[29] The temperature of the reaction was maintained at -15°. Color Test II was negative after 2 hours. Then there were slowly added 50 ml. of an ethereal solution containing 9.60 g. (0.038 mole) of diphenyldichlorosilane. The reaction mixture was allowed to come to room temperature and stirred overnight. Color Test

I was negative at that time and a white solid was suspended in the reaction mixture. Hydrolysis with 200 ml. of water resulted in two clear, liquid layers. The ether layer was separated and a solid began to precipitate from it. There was filtered off 8.4 g. of a white solid melting over the range 156-159°. The ether layer was dried and distilled. There was recovered 4.5 g. of p-bromophenyl phenyl ether. In addition the residue contained 1.1 g. of a white solid melting over the range 154-158°. The combined product was recrystallized from a mixture of dioxane and 95% ethanol. There was obtained 7.20 g. (36.8%) of pure product melting at 162-163°.

Anal. Calcd. for $C_{36}H_{28}O_2Si$: Si, 5.39. Found: Si, 5.34, 5.40.

Phenyl-tris-(p-phenoxyphenyl)-silane

To 110 ml. of an ethereal solution containing 0.0895 mole of n-butyllithium (at -15°) were slowly added 75 ml. of an ethereal solution containing 22.4 g. (0.090 mole) of p-bromophenyl phenyl ether[29]. Color Test II was negative after 4 hours. There were then slowly added 25 ml. of an ethereal solution containing 5.30 g. (0.025 mole) of phenyltrichlorosilane. Color Test I was immediately negative.

The reaction mixture was allowed to come to room temperature under constant stirring. Hydrolysis with 200 ml. of water gave an insoluble white product (10.1 g.) melting over the range 160-180°. The ether layer was separated, dried and distilled. There was isolated 3.3 g. of a white solid melting at 158-159°. The combined solids were recrystallized from a mixture of dioxane and 95% ethanol to give 10.2 g. (67.1%) of pure product melting at 149-150°.

Anal. Calcd. for $C_{42}H_{32}O_3Si$: Si, 4.57. Found: Si, 4.51, 4.61.

Tetrakis-(p-phenoxyphenyl)-silane

To 115 ml. of an ethereal solution containing 0.095 mole of n-butyllithium (at -15°) were slowly added 75 ml. of an ethereal solution containing 23.7 g. (0.095 mole) of p-bromophenyl phenyl ether[29]. Color Test II was negative after 2 hours stirring. There were then slowly added 25 ml. of an ethereal solution containing 3.4 g. (0.020 mole) of silicon tetrachloride. The temperature of the mixture was allowed to rise slowly and then brought to reflux for 4 hours. Color Test I was negative at that time. The white reaction mixture was cooled to room temperature and hydrolyzed with 175 ml. of water. A white solid, suspended between the organic and aqueous layers was filtered off. There was obtained 10.7 g. of material melting over the range 200-204°. Separation, drying and distillation of the ether solvent gave an oily liquid having the odors of n-butyl bromide and p-bromophenyl phenyl ether. The collected solid was recrystallized from ethyl acetate. There was finally obtained 8.21 g. (58.3%) of the desired product melting at 204°.

Anal. Calcd. for $C_{48}H_{36}O_4Si$: Si, 3.99. Found: Si, 3.95, 3.90.

Tris-(p-phenoxyphenyl)-n-dodecylsilane

A solution of 47.5 g. (0.190 mole) of p-bromophenyl phenyl ether[29] in 75 ml. of ether was added to 210 ml. of an ethereal solution containing 0.187 mole of n-butyllithium. The temperature of the reaction mixture was maintained at -15° throughout the addition. After 2 hours stirring, Color Test II was negative. There was then added a solution of 17.6 g. (0.057 mole) of n-dodecyltrichlorosilane in 50 ml. of ether. The temperature was then raised to reflux and maintained there for 18 hours. A white precipitate slowly formed during this time. Color Test I was then negative. Hydrolysis with 200 ml. of water resulted in two clear layers. The ether fraction was separated, dried and then distilled. The product obtained was a highly-viscous, amber oil which resisted all crystallization attempts by use of various solvents. The oil was finally distilled in a temperature range of 315-320° at 0.004 mm. in a Hickman molecular still. Total weight of this liquid was 10.3 g. (25.2%).

Anal. Calcd. for $C_{48}H_{52}O_3Si$: Si, 3.99. Found: Si, 4.03, 4.09.

Tris-(p-phenoxyphenyl)-silane (attempted)

Run I. There were added to 4.5 g. (0.18 mole) of magnesium turnings suspended in 100 ml. of ether 50 drops of an ethereal solution containing 45.0 g. (0.180 mole) of p-bromophenyl phenyl ether[29] and a small crystal of iodine. After 15 minutes, the mixture became turbid and some reflux was noted. The remaining 75 ml. of solution were added at a rate sufficient to maintain gentle reflux. After 2 hours stirring, there was obtained a 94% yield of the Grignard reagent as determined by the simple acid titration. The reaction mixture was cooled to 0° and 20 ml. of an ethereal solution containing 6.8 g. (0.50 mole) of trichlorosilane[30] were slowly added. Immediate reaction was noted by the formation of a white precipitate. Several hours stirring were necessary to give a negative Color Test I. As the temperature of the mixture was gradually raised to reflux, the solution turned from a pale-amber to a deep-brown color. The reaction flask was cooled very quickly after reaching the reflux temperature. Hydrolysis with 100 ml. of 3 N hydrochloric acid resulted in a yellow ether layer and dissolution of the solid. The organic solvent was separated, dried and distilled. The residue consisted of a deep-brown, viscous oil. Vacuum distillation of the material gave the following fractions:

1. Colorless viscous liquid, b.p. 65-85° (1.0 mm.)
2. Amber viscous liquid, b.p. 85-92° (1.5 mm.)

Neither fraction could be crystallized. Infrared data[31] failed to disclose the presence of the silicon-hydrogen bond in either fraction.

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[30] The procedure was in essential accordance with that of F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, ibid., 69, 2108 (1947) for the addition of trichlorosilane to a Grignard reagent.

[31] The author is grateful to Drs. V. A. Fassel, Marvin Margoshes, Messrs. Richard M. Hedges, Robert D. Kross and Robert McCord of the Institute for Atomic Research for the determination of and assistance in the interpretation of the infrared spectra.

Run II. The same quantities of all reagents were employed. One modification was that the temperature of the reaction mixture was not raised above 28°. The other was that the volume of the solution was concentrated to 100 ml., with the aid of an aspirator, after the trichlorosilane had been added. Results essentially the same as those for Run I were obtained.

Run III. The additional modification employed in this experiment was that the temperature of the p-phenoxyphenylmagnesium bromide solution was cooled to -25° prior to the addition of the trichlorosilane solution. None of the desired product was isolated.

Diphenyl-bis-(9-fluorenyl)-silane

To 250 ml. of an ethereal solution containing 21.2 g. (0.127 mole) of fluorene[32] were slowly added 150 ml. of an ethereal solution containing 0.127 mole of phenyllithium. The solution became yellow, then orange during the addition. There were then slowly added 75 ml. of an ethereal solution containing 12.7 g. (0.050 mole) of diphenyldichlorosilane. The reaction mixture became a mustard color during this

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[32] K. Ziegler and L. Jakob, Ann., 511, 45 (1934).

addition. Color Test I was negative after refluxing overnight.

The reaction mixture was hydrolyzed with 250 ml. of water. The ether layer was separated, dried and distilled. The residual white solid was recrystallized from a mixture of dioxane and 95% ethanol. There was isolated 2.4 g. of a white solid melting over the range 225-240°. Several recrystallizations did not narrow the melting point range. Concentration of the original recrystallizing solvent gave 2.7 g. (10.6%) of pure product melting at 270°.

Anal. Calcd. for $C_{38}H_{28}Si$: Si, 5.47. Found: Si, 5.55, 5.50.

Phenyl-tris-(9-fluorenyl)-silane

To an ethereal solution of 12.3 g. (0.075 mole) of fluorene in 150 ml. of ether were rapidly added 122 ml. of a solution containing 0.075 mole of phenyllithium[32]. The mixture became yellow and then rust-red during the addition. After 4 hours of reflux, there was slowly added a solution of 4.88 g. (0.023 mole) of phenyltrichlorosilane in 25 ml. of ether. Color Test I was found to be negative after 8 hours of reflux. Hydrolysis with 250 ml. of water resulted in the suspension of a white solid between the ether and water layers. The solid, filtered and air-dried, weighed 10.0 g. and melted over the range 290-318°. The ether layer was separated, dried and distilled. There was isolated 2.1 g. of rust-colored solid melting over the range 152-196° and having an odor similar to fluorene. This material was not further purified.

The solid originally collected was recrystallized from a mixture of ethyl acetate and 95% ethanol. There was finally obtained 6.6 g. (46.6%) of desired product melting at 333-334°.

Anal. Calcd. for $C_{45}H_{32}Si$: Si, 4.66. Found: Si, 4.62, 4.50.

Tetrakis-(9-fluorenyl)-silane (attempted)

Run I. To 150 ml. of an ethereal solution containing 13.0 g. (0.078 mole) of fluorene[32] were added 96 ml. of an ethereal solution containing 0.078 mole of phenyllithium. The resultant rust-red solution was refluxed for 4 hours after completion of the addition. There were then added to the mixture, at room temperature, 50 ml. of an ethereal solution of 2.90 g. (0.017 mole) of silicon tetrachloride. A reaction was immediately noticed as the mixture began to reflux. The color became yellow and remained so during 24 hours of reflux. The yellow solid which precipitated was filtered and washed with water. A small quantity held in a Bunsen flame gave the crimson color of lithium. Further washing with water resulted in a dark-brown, glasslike solid.

The ether layer was hydrolyzed with 200 ml. of water. After drying and distilling the organic solvent, there remained 16.5 g. of a dark-brown, glass-like solid. No solvents produced any change in this solid.

Run II. In another preparation, the silicon tetrachloride was added very slowly to the reaction mixture at 0°. The solid finally isolated had the physical appearance and properties described above.

Diphenyl-bis-(*m*-trifluoromethylphenyl)-silane

To a solution of 0.087 mole of *n*-butyllithium in 112 ml. of ether at -15° was slowly added an ethereal solution of 19.5 g. of *m*-trifluoromethylbromobenzene in 50 ml. of ether[33]. The solution turned brown during the addition. Color Test II was negative after 2 hours. There were then added 50 ml. of an ethereal solution containing 8.85 g.

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[33] H. Gilman and L. A. Woods, *J. Am. Chem. Soc.*, *66*, 1981 (1944).

(0.035 mole) of diphenyldichlorosilane. The temperature was allowed to rise slowly, and then heat was applied to bring the solution to reflux. After 24 hours, Color Test I was doubtful. Hydrolysis with 150 ml. of water resulted in a brown ether layer and colorless, aqueous layer. The ether fraction was separated, dried and distilled. There remained an oil which became a semi-solid on cooling in an ice bath. Stirring with methanol gave a white solid melting over the range 93-96°. Recrystallization from the same solvent yielded 9.1 g. (56%) of desired product melting at 97-98°.

Anal. Calcd. for $C_{2\overset{6}{\cancel{4}}}H_{18}F_6Si$: C, 66.0; H, 3.82. Found: C, 65.6, 65.55; H, 3.86, 3.92.

Phenyl-tris-(m-trifluoromethylphenyl)-silane

To 121 ml. of an ethereal solution containing 0.094 mole of n-butyllithium at -15° were slowly added 55 ml. of an ethereal solution containing 21.2 g. (0.094 mole) of m-trifluoromethylbromobenzene[33]. Color Test II was negative after 2 hours. At the same temperature was then added a solution of 5.71 g. (0.027 mole) of phenyltrichlorosilane in 25 ml. of ether. Color Test I was negative after 24 hours of reflux. The reaction mixture was hydrolyzed with

150 ml. of water. After separating, drying and distilling the organic layer, there remained an oily residue. This product crystallized on standing overnight. It weighed 7.4 g. and melted over the range 78-81°. Several recrystallizations from methanol gave 6.3 g. (43.4%) of pure product melting at 81°.

Anal. Calcd. for $C_{2\overset{7}{\cancel{4}}}H_{17}F_9Si$: C, 60.0; H, 3.15. Found: C, 60.09, 60.24; H, 3.23, 3.20.

Tetrakis-(m-trifluoromethylphenyl)-silane

To 0.190 mole of n-butyllithium in 205 ml. of ether at -15° were added 50 ml. of a solution containing 42.7 g. (0.190 mole) of m-trifluoromethylbromobenzene[33]. After 2 hours of stirring, Color Test II was negative. There was then added a solution of 7.48 g. (0.044 mole) of silicon tetrachloride in 25 ml. of ether. As the temperature of the reaction mixture was brought to reflux, a cream-colored precipitate was noted. Total reflux time was 24 hours. Hydrolysis with 250 ml. of water produced a gelatinous layer between the ether and water. The organic layer was separated, dried and distilled. There remained a "wet" solid which melted over the range 100-103°. After several washings with methanol and recrystallization from petroleum ether (b.p. 60-70°), there was isolated 11.1 g. (41.7%) of desired product melting at 102-103°.

Anal. Calcd. for $C_{\overset{28}{\cancel{24}}}H_{16}F_{12}Si$: C, 55.4; H, 2.63. Found: C, 55.47, 55.43; H, 2.67, 2.66.

Tris-(*m*-trifluoromethylphenyl)-silane

Thirty drops of an ethereal solution of 56.4 g. (0.250 mole) of *m*-trifluoromethylbromobenzene were added to a suspension of 6.1 g. (0.25 mole) of magnesium and a small crystal of iodine. The solution became turbid after several minutes and the remaining 100 ml. were added at a rate sufficient to maintain gentle reflux. After 2 hours of stirring, a simple acid titration gave an 81% yield. The Grignard reagent was cooled to 0° and 50 ml. of an ethereal solution containing 8.10 g. (0.060 mole) of trichlorosilane[34] were slowly added. Then the temperature was allowed to rise slowly and heat applied to bring the reaction mixture to reflux. Color Test I was negative at that time. Hydrolysis with 100 ml. of 2 N hydrochloric acid resulted in two colorless layers. The ether fraction was separated, dried and

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[34] R. A. Benkesser and F. J. Riel, *ibid.*, *73*, 3472 (1951).

distilled. A deep-brown, viscous oil remained. Vacuum distillation gave the following fractions:

1. Colorless liquid, 4.3 g., b.p. 32-50° (0.45 mm.)
2. Colorless liquid, 25.4 g., b.p. 147-150° (0.05 mm.)

Fraction 2, on treatment with aqueous-alcoholic potassium hydroxide[35], evolved a gas (H_2) indicating the presence of the silicon-hydrogen bond. The liquid has the physical constants, n_D^{20} 1.4948 and d_{20}^{20} 1.3500. There was obtained 25.4 g. (92.2%).

__Anal.__ Calcd. for $C_{21}H_{13}F_{\overset{7}{\cancel{4}}}Si$: C, 54.4; H, 2.81; MR_D[36], 100.1. Found: C, 54.12, 54.25; H, 2.88, 2.91; MR_D, 101.3.

__Tris-(m-trifluoromethylphenyl)-p-phenoxyphenylsilane (attempted)__

There was slowly added a solution containing 5.48 g. (0.022 mole) of __p__-bromophenyl phenyl ether[29] in 25 ml. of ether to 60 ml. of an ethereal solution containing 0.022 mole of __n__-butyllithium at -15°. A negative Color Test II was obtained after 2 hours. To this organolithium reagent were then added 25 ml. of an ethereal solution containing

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[35] F. P. Price, __ibid.__, __69__, 2600 (1947).

[36] E. L. Warrick, __ibid.__, __68__, 2455 (1946).

7.35 g. (0.0158 mole) of tris-(m-trifluoromethylphenyl)-silane[37]. The reaction mixture was then refluxed for 24 hours. The resultant turbid solution was hydrolyzed with 100 ml. of water. Considerable frothing and bubbling was noted during the hydrolysis. A white solid formed during the water addition, but dissolved on further stirring. Separation, drying and distillation of the ether solvent gave a small quantity of a viscous oil. Attempts to crystallize this material by treatment with various solvents failed. There was an odor similar to that of diphenyl ether associated with the product. Vacuum distillation procedures caused decomposition of the residue without obtaining any distillate.

Phenyl-tris-(m-trifluoromethylphenyl)-silane (attempted)

To 0.010 mole of phenyllithium in 50 ml. of ether was added a solution containing 4.0 g. (0.009 mole) of tris-(m-trifluoromethylphenyl)-silane in 50 ml. of ether[33]. The reaction mixture was then refluxed for 24 hours. Color Test I was faintly positive at that time. The turbid

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[37] H. Gilman and S. P. Massie, ibid., 68, 1128 (1946); R. N. Meals, ibid., 68, 1880 (1946).

solution was hydrolyzed with 100 ml. of water. A gray solid, formed during the hydrolysis, dissolved on further stirring. The ether fraction was separated, dried and distilled. The oily residue had an odor similar to that of benzene. Further distillation did afford several grams of liquid boiling at 80°. All attempts to crystallize the residual viscous, semi-solid were unsuccessful.

Triphenyl-m-tolylsilane

Method A. To 0.052 mole of m-tolyllithium[38] in 75 ml. of ether were slowly added 100 ml. of an ethereal solution containing 13.5 g. (0.046 mole) of triphenylchlorosilane. The mixture became a rust color on completion of the addition. The temperature of the solution was raised to reflux and maintained there for 6 hours. Color Test I was then negative. Hydrolysis with 150 ml. of water turned the ether solvent a pale-amber color. The organic layer was separated, dried and distilled. There remained 14.8 g. of a white solid melting over the range 143-148°. After recrystallization from petroleum ether (b.p. 60-70°), there was obtained 12.3 g. (77%) of desired product melting at 150-151°.

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[38] Kindly furnished by Dr. K. Oita.

Anal. Calcd. for $C_{25}H_{22}Si$: Si, 8.00. Found: Si, 8.02, 8.08.

Method B. To a stirred suspension of 0.49 g. (0.066 g. atom) of lithium wire (cut into pieces less than 1 cm. in length) in 50 ml. of ether were added 25 ml. of an ethereal solution containing 5.13 g. (0.030 mole) of m-bromotoluene[39]. The addition was carried out at a rate sufficient to maintain gentle reflux. After stirring for 1 hour, there was obtained a 93% yield as determined by simple acid titration. To this lithium reagent were added 50 ml. of an ethereal solution containing 7.27 g. (0.028 mole) of triphenylsilane[40]. The reaction mixture began to reflux and a white precipitate formed during this addition. Color Test I was negative after 2 hours. Hydrolysis with 75 ml. of water resulted in the dissolution of the solid. The ether layer was separated, dried and distilled. The residual white solid weighed 7.7 g. and melted over the range 134-142°. Several recrystallizations from petroleum ether (b.p. 60-70°) afforded 5.8 g. (59%) of desired product

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[39] H. Gilman, E. A. Zoellner and W. M. Selby, J. Am. Chem. Soc., 55, 1252 (1933).

[40] W. H. Nebergall and O. H. Johnson, ibid., 71, 4022 (1949).

melting at 149-150°. A mixture of this material and an authentic sample[41] melted at 149-150°.

Diphenyl-bis-(m-tolyl)-silane

To 0.075 mole of m-tolyllithium[38] in 95 ml. of ether was added a solution of 8.85 g. (0.035 mole) of diphenyldichlorosilane in 50 ml. of ether. Color Test I was negative after 6 hours of reflux. The reaction mixture changed from a rust-red to pale-amber color on hydrolysis with 125 ml. of water. The ether layer was separated, dried and distilled. The remaining white solid weighed 11.6 g. and melted over the range 112-116°. Several recrystallizations from a mixture of 95% ethanol and benzene yielded 9.7 g. (76.5%) of pure product melting at 119-120°.

Anal. Calcd. for $C_{26}H_{24}Si$: Si, 7.69. Found: Si, 7.71, 7.74.

Phenyl-tris-(m-tolyl)-silane

To 0.096 mole of m-tolyllithium[38] in 110 ml. of ether were slowly added 50 ml. of an ethereal solution containing

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[41] This Thesis, p. 42.

6.36 g. (0.030 mole) of phenyltrichlorosilane. After stirring at reflux temperature for 6 hours, Color Test I was found to be negative. Hydrolysis with 150 ml. of water resulted in a pale-amber organic layer. The ether fraction was then separated, dried and distilled. A white solid weighing 9.2 g. and melting over the range 120-126° remained. Several recrystallizations from a mixture of 95% ethanol and benzene afforded 8.6 g. (76%) of desired compound melting at 128-129°.

Anal. Calcd. for $C_{27}H_{26}Si$: Si, 7.40. Found: Si, 7.41, 7.48.

Tetrakis-(m-tolyl)-silane

A solution of 5.45 g. (0.035 mole) of silicon tetrachloride in 50 ml. of ether was added to 150 ml. of an ethereal solution containing 0.154 mole of m-tolyllithium[38]. The rust-red mixture was refluxed for 6 hours. Color Test I was negative after that time. The ether layer became pale-yellow on hydrolysis with 200 ml. of water. After separation and drying of the organic layer, it was distilled. There remained 9.2 g. of a white solid melting over the range 142-149°. Several recrystallizations from a mixture of 95% ethanol and benzene gave 8.9 g. (65%) of pure product melting at 155-156°.

Anal. Calcd. for $C_{28}H_{28}Si$: Si, 7.15. Found: Si, 7.24, 7.19.

Trimethyl-2-biphenylylsilane

There was slowly added to a stirring suspension of 1.06 g. (0.154 g. atom) of lithium wire (cut into pieces of less than 1 cm. in length) in 75 ml. of ether a solution of 16.3 g. (0.070 mole) of 2-bromobiphenyl[42] in 35 ml. of ether. Heating to reflux was required to start the reaction. Once underway, the formation of the organolithium compound evolved enough heat to maintain reflux, simple acid titration showed a 95% yield of 2-biphenylyllithium. To this organometallic reagent at 0° were added 25 ml. of an ethereal solution containing 6.0 g. (0.055 mole) of trimethylchlorosilane. The color of the reaction mixture became yellow during this addition and a precipitate slowly appeared. Color Test I gave a negative result after 12 hours of reflux. On cooling, the suspension was hydrolyzed

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[42] K. Oita, Unpublished Ph.D. Thesis, Iowa State College Library, 1955.

with 100 ml. of water. The ether layer was separated, dried and distilled. The remaining viscous oil gave the following fractions on vacuum distillation:

1. Biphenyl, 1.2 g., b.p. 55-88° (0.075 mm.)
2. Trimethyl-2-biphenylylsilane, 10.2 g., b.p. 97-102° (0.06 mm.)

The physical properties of Fraction 2 are n_D^{20} 1.5655, and d_{20}^{20} 0.9750. The yield of desired product was 82.6%.

Anal.[43] Calcd. for $C_{15}H_{18}Si$: Si, 12.4; MR_D 75.03. Found: Si, 12.1, 12.2; MR_D 75.5.

Bis-(p,p'-trimethylsilyl)-diphenyl ether

To 195 ml. of an ethereal solution containing 0.181 mole of n-butyllithium at 0° was slowly added a solution consisting of 28.8 g. (0.092 mole) of di-p-bromophenyl ether[29] in 128 ml. of ether. Color Test II was negative after 4 hours stirring. There were then added 50 ml. of an ethereal solution containing 15.3 g. (0.140 mole) of trimethylchlorosilane. The reaction mixture was then

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[43] Analysis for silicon in molecules possessing the easily cleaved trimethylsilyl-group was carried out by the procedure of C. L. Tseng and T. Y. Chao, Science Repts. Natl. Univ. Peking, 1, No. 4, 21-37 (1936). [Original not available for examination; abstracted in C. A., 31, 655 (1937).]

refluxed for 24 hours. Color Test I was negative at that time. Hydrolysis was carried out with 250 ml. of water. A white solid, formed during this process, was dissolved on continued stirring. The ether fraction was separated, dried and distilled. The residual oil gave two fractions on vacuum distillation.

1. Colorless liquid having the odor of diphenyl ether, b.p. 80-110° (0.01 mm.)
2. Bis-(*p*,*p*'-trimethylsilyl)-diphenyl ether, 21.3 g., b.p. 119-125° (0.02 mm.)

The desired product (Fraction 2) has the following constants: n_D^{20} 1.5430 and d_{20}^{20} 1.0251. The yield of pure product was 95.6%.

Anal.[43] Calcd. for $C_{18}H_{26}OSi_2$: Si, 17.81; MR_D 96.5. Found: Si, 17.5, 17.7; MR_D, 96.2.

Tris-(*p*-trimethylsilylphenyl)-silane

To a suspension of 18.7 g. (0.770 g. atom) of magnesium turnings in 150 ml. of ether and a small crystal of iodine was added a solution of 171 g. (0.750 mole) of trimethyl-*p*-bromophenylsilane[44] in 110 ml. of ether. The reaction

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[44] H. Gilman and H. W. Melvin, Jr., *J. Am. Chem. Soc.*, *72*, 995 (1950).

began after several minutes (as evidenced by a turbidity of the suspension) and the addition rate was controlled to maintain a gentle reflux. Simple acid titration, after 2 hours at the boiling temperature, gave a 93.5% yield. The reaction mixture was cooled to 0° and there was added a solution of 27.0 g. (0.20 mole) of trichlorosilane in 50 ml. of ether. The addition was carried out very slowly because of the violent reaction noted as each drop hit the Grignard reagent. The reaction mixture became a white, pasty mass as the addition of the silane neared completion. Color Test I was found to be negative after 4 hours reflux. A large quantity of gelatinous, white solid remained after hydrolysis with 250 ml. of 3 N hydrochloric acid. This material was filtered off and air-dried. The product (54.6 g.) melted over the range 154-158°. Separation, drying and distillation of the ether layer gave 10.2 g. of product melting over the range 156-159°. The combined solids were recrystallized from a mixture of 95% ethanol and ethyl acetate. There was finally isolated 61.3 g. (64.8%) of desired compound melting at 159-160°.

Anal.[43] Calcd. for $C_{27}H_{40}Si_4$: Si, 23.5. Found: Si, 24.1, 23.8.

Tris-(p-trimethylsilylphenyl)-p-phenoxyphenylsilane (attempted)

To 0.024 mole of n-butyllithium in 35 ml. of ether at -15° were slowly added 30 ml. of a solution containing 7.45 g. (0.030 mole) of p-bromophenyl phenyl ether[29]. Color Test II was negative after 3 hours stirring. To the organolithium reagent at 0° was then added a suspension consisting of 8.0 g. (0.017 mole) of tris-(p-trimethylsilylphenyl)-silane in 50 ml. of ether. After 18 hours of reflux, Color Test I was found to be negative. Hydrolysis with 100 ml. of water resulted in two, colorless layers. The ether fraction was separated, dried and distilled. There remained 6.8 g. of a white solid melting over the range 150-154°. A strong odor resembling diphenyl ether was associated with the solid. Recrystallization of the solid from a mixture of 95% ethanol and ethyl acetate gave a 70% recovery of tris-(p-trimethylsilylphenyl)-silane, identified by the mixed melting point method. No other compound was isolated.

Tris-(p-trimethylsilylphenyl)-2-biphenylylsilane (attempted)

To 110 ml. of an ethereal solution containing 0.168 mole of 2-biphenylyllithium[42] were added 100 ml. of an ethereal suspension containing 0.0168 mole of tris-(p-trimethylsilylphenyl)-silane. This mixture was brought to reflux and that temperature maintained for 40 hours. Color Test I was faintly positive at that time. The deep-brown solution was hydrolyzed with 200 ml. of water. Separation, drying and distillation of the solvent gave a tan solid and a dark-brown oil. The solid was collected and the oil treated with a mixture of 95% ethanol and ethyl acetate. This resulted in the solidification of the oil. Both of the solids melted over the range 149-156°. Recrystallization from the mixed solvents gave a 62% recovery of the starting organosilicon compound.

Tris-(p-trimethylsilylphenyl)-m-trifluoromethylphenylsilane (attempted)

To 190 ml. of an ethereal solution containing 0.174 mole of n-butyllithium were added 50 ml. of an ethereal solution containing 40.5 g. (0.180 mole) of m-trifluoromethylbromobenzene[33]. After stirring for 2 hours at 0°, Color Test II was negative. There was then slowly added at the same temperature, a suspension of 8.0 g. (0.017 mole) of tris-(p-trimethylsilylphenyl)-silane in 100 ml. of ether. The mixture was brought to reflux and maintained there for 40 hours. Color Test I was faintly positive at that time. Hydrolysis with 150 ml. of water resulted in considerable frothing and bubbling. The ether fraction was then separated, dried and distilled. There remained a deep-maroon liquid. Vacuum distillation of this residue gave the following fractions:

1. *n*-butyl bromide, 5.5 g., b.p. 35-41° (0.17 mm.)
2. Colorless liquid, 4.6 g., b.p. 49-55° (0.17 mm.)
3. Colorless liquid, 6.1 g., b.p. 74-115° (0.12 mm.)

All attempts to crystallize Fractions 2 and 3 were unsuccessful. Neither of them was further identified. There was no recovery of the starting silane as in the previously described experiments involving the use of the initial tris-(*p*-trimethylsilylphenyl)-silane.

Tris-(*p*-trimethylsilylphenyl)-*m*-tolylsilane (attempted)

Run I. To a stirred suspension of 0.198 g. (0.0308 mole) of lithium wire (cut into pieces less than 1 cm. in length) in 50 ml. of ether was added a solution containing 2.4 g. (0.014 mole) of *m*-bromotoluene[39] in 20 ml. of ether. The mixture was refluxed for 1 hour and stirred for an additional hour. Simple acid titration gave a yield of 91%. There were then added 50 ml. of an ethereal suspension containing 5.5 g. (0.11 mole) of tris-(p-trimethylsilylphenyl)-silane. No visible reaction occurred during the addition. The mixture was brought to reflux and maintained at that temperature for 6 hours. Color Test I was negative. Hydrolysis with 100 ml. of water gave two colorless layers. The ether fraction was separated, dried and distilled. There remained 4.2 g. of a white solid melting over the range 140-146°. Several recrystallizations from a mixture of 95% ethanol and ethyl acetate afforded 3.6 g. of a white solid melting at 159-160°. A mixed melting point carried out on a mixture of this material and an authentic sample of the starting silane showed no depression. The recovery was 64.4%. No other compound was isolated.

Run II. This experiment was carried out with the same quantities as in Run I. The modification in the technique was that a benzene solution (50 ml.) of tris-(p-trimethylsilylphenyl)-silane replaced the ether suspension. After completion of the addition of the silane, the reaction mixture was heated and the ether (present from the m-tolyllithium preparation) was distilled. Then the remaining benzene solution was refluxed for 4 hours. Hydrolysis with 50 ml. of water was followed by the separation, drying and distillation of the benzene layer. There remained 5.4 g. of a crystalline solid melting over the range 133-139°.

One recrystallization of this product from a mixture of 95% ethanol and ethyl acetate afforded 4.7 g. of a solid melting over the range 138-159°. Further recrystallizations did not narrow the melting point range. All attempts to separate the probable mixture of compounds by fractional crystallization techniques were unsuccessful.

Phenyl-tris-(p-trimethylsilylphenyl)-silane

To 25 ml. of a benzene solution containing 3.5 g. (0.0074 mole) of tris-(p-trimethylsilylphenyl)-silane was added a solution of a 0.015 mole of phenyllithium in 60 ml. of ether. Color Test I was negative immediately after completion of the addition. Hydrolysis with 75 ml. of water resulted in two colorless layers. The organic fraction was separated, dried and distilled. There remained 3.3 g. of a white solid melting over the range 141-183°. Fractional crystallization from a mixture of 95% ethanol and ethyl acetate gave 2.1 g. of a white solid melting at 190-191°, and 1.1 g. (31.5% recovery) of starting silane. The compound melting at 190-191° was identified as phenyl-tris-(p-trimethylsilylphenyl)-silane[45] by the method of mixed melting points. The yield of desired product was 52%.

Tris-(p-trimethylsilylphenyl)-n-dodecylsilane

Method A. To a stirred suspension of 1.5 g. (0.22 g. atom) of lithium wire (cut into pieces less than 1 cm. in length) in 50 ml. were added 75 ml. of an ethereal solution containing 2.14 g. (0.0935 mole) of trimethyl-p-bromophenylsilane[44]. The reaction began in several minutes as evidenced by an increasing turbidity of the reaction mixture. The remaining solution was added at such a rate that the gentle reflux never stopped. (This control must be carefully maintained as cessation of reflux may entail the termination of the formation of the lithium reagent. It is difficult to resume the reaction once it has stopped.) The solution became pink, then red-brown during the addition. After 2 hours reflux, there was obtained only a 59% yield of p-trimethylsilylphenyllithium as determined by the simple acid titration method.

There was then added to the organolithium reagent at

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[45] Dr. R. Fuchs, unpublished studies, Iowa State College. This compound was prepared by the reaction between phenyltrichlorosilane and p-trimethylsilylphenyllithium.

0° a solution of 4.55 g. (0.0150 mole) of _n_-dodecyltrichlorosilane in 50 ml. of ether. The temperature of the resultant solution was raised to reflux and maintained there for 18 hours. (The nitrogen supply ran out during the night. There was an inert atmosphere for at least 8 hours.) Color Test I was negative at that time. Hydrolysis with 150 ml. of water resulted in pale-brown ether layer and a turbid, deep-brown aqueous layer. The organic fraction was separated, dried and distilled. There remained a brown liquid. Vacuum distillation of this material gave the following fractions:

1. Colorless liquid, 1.2 g., b.p. 38-42° (0.1 mm.)
2. Trimethyl-_p_-bromophenylsilane, 4.7 g., b.p. 44-46° (0.05 mm.)

There remained a considerable quantity of a highly-viscous oil which did not distill under these conditions. Fraction 2 had the characteristic odor of the starting silane and the same refractive index, 1.5280 at 20°. Total recovery was 22%. Distillation of the high-boiling residue in a Hickman molecular still gave 6.3 g. of a pale-yellow oil boiling over the range 210-218° at 0.005 mm. After two days there were signs of crystallization taking place in the oil. The entire mass was a "wet" solid one month later. The product melted over the range 68-74°.

Method B. To a stirred suspension of 0.38 g. (0.055 g. atom) of lithium wire (cut into pieces of less than 1 cm. in length) in 50 ml. of ether were added 15 drops of a solution of 6.25 g. (0.025 mole) of n-dodecylbromide in 25 ml. of ether. As soon as a turbidity developed in the solution, the temperature of the mixture was lowered to -20° by means of a Dry Ice-acetone bath. The remainder of the ethereal solution was added over a period of 30 minutes. The temperature was now raised to 0° and maintained there for 2 hours. The yield of n-dodecyllithium, as determined by the double titration procedure was 85%.

To this organometallic reagent, at 0°, were slowly added 75-ml. of a benzene solution containing 11.4 g. (0.024 mole) of tris-(p-trimethylsilylphenyl)-silane. The reaction mixture was then heated to the reflux temperature and maintained there for 24 hours. Color Test I was negative at that time. Hydrolysis with 150 ml. of water caused the evolution of a gas. The resultant ether fraction was separated, dried and distilled. There remained a light-brown oil. This material became a "wet" solid melting over the range 68-75°.

All attempts to recrystallize the product from either Method A or B resulted in an oil which could not be solidified.

Anal. Calcd. for $C_{39}H_{64}Si_4$; Si, 17.4. Found: Si, 16.7, 16.9.

Tris-(p-trimethylsilylphenyl)-n-octadecylsilane (attempted)

To 2.6 g. (0.34 g. atom) of lithium wire (cut into pieces less than 1 cm. in length) suspended in 150 ml. of ether were added 10 ml. of an ethereal solution containing 30.0 g. (0.131 mole) of trimethyl-p-bromophenylsilane[44]. After the reaction had begun, as indicated by an increasing turbidity of the stirred suspension, the remaining 110 ml. of solution were added at a rate sufficient to maintain gentle reflux. The resultant pink-brown solution was stirred for 30 minutes after completion of the addition. Analysis by the simple acid titration procedure gave a 68% yield. To the organolithium reagent, at room temperature, was then slowly added a solution containing 11.4 g. (0.0297 mole) of trichloro-n-octadecylsilane in 75 ml. of ether. The color of the solution became gray-tan on completion of the addition. After 6 hours of reflux, Color Test I was found to be negative. There was some reaction noted during hydrolysis of the reaction mixture with 250 ml. of water. A solid, formed during the addition of the trichloro-n-octadecylsilane, was dissolved during this procedure. The ether layer was then separated, dried and distilled. There remained a turbid, yellow liquid. Vacuum distillation of the residue gave 7.3 g. (24.3%) of trimethyl-p-bromophenylsilane and a highly viscous semi-solid. All attempts to induce crystallization of this mass failed. Distillation in a Hickman molecular still gave 4.2 g. of pale-yellow liquid boiling over the range 126-201° at 0.005 mm. This material nor the undistilled glasslike residue could be further identified.

Tris-(p-bromophenyl)-silane

To a stirred suspension of 7.6 g. (0.31 g. atom) of magnesium turnings in 100 ml. of ether were added 10 ml. of a solution of 72.5 g. (0.307 mole) of p-dibromobenzene[46] in 250 ml. of ether. After the reaction had begun, as evidenced by an increasing turbidity of the reaction mixture, the remainder of the solution was added at rate sufficient to maintain gentle reflux. Total addition time was 2 hours. Simple acid titration gave a 90% yield. To the p-bromophenylmagnesium bromide at room temperature were then added 50 ml. of an ethereal solution containing 12.0 g. (0.089

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[46] E. A. Zoellner, Unpublished Ph.D. thesis, Iowa State College Library, 1933.

mole) of trichlorosilane. This solution was added dropwise because of the violent reaction between the Grignard agent and this silane. After completion of the addition, the mixture was refluxed for 1 hour. Color Test I was positive at that time. Hydrolysis was carried out with 150 ml. of 3 N hydrochloric acid cooled to 0°. The ether layer was then separated, dried and distilled. There remained a highly-viscous, tan oil which did not crystallize on treatment with 95% ethanol. This solvent was distilled and the residue vacuum distilled. There sublimed in the apparatus 6.6 g. of a white solid identified as p-dibromobenzene by the method of mixed melting points. This was a 9.1% recovery. The remaining liquid was then distilled over the range 175-192° at 0.02 mm. This product became a semi-solid on standing. Treatment with hot, 95% ethanol left a small quantity of an immiscible oil. The solvent was separated and cooled. There was precipitated 6.5 g. (14.9%) of white needles melting at 107-108°. Treatment of this product with aqueous-alcoholic potassium hydroxide evolved a gas (H_2) indicating the presence of silicon-hydrogen bond[35]. The small quantity of oil was not further identified.

Anal. Calcd. for $C_{12}H_{13}Br_3Si$: Si, 5.61. Found: Si, 5.55, 5.51.

Tris-(triphenylgermyl)-silane

Run I. Into 250 ml. of anhydrous ammonia (at -45 to -55°) was placed 10.0 g. (0.0165 mole) of hexaphenyldigermane. To this stirred suspension was added 0.76 g. (0.033 g. atom) of sodium metal cut into small pieces[47]. As the sodium dropped into the solvent, an intense blue color developed. After several minutes, the color changed to yellow. The reaction mixture was yellow after all the sodium metal had been added. The Dry Ice-acetone bath was removed and the ammonia allowed to evaporate. The residue was then heated (80-100°) and a vacuum pump attached to the system. The pump was run for 15 minutes at that temperature. The color of the remaining solid became a light-gray. There were then added 200 ml. of ether. To the stirred suspension were added 25 ml. of an ethereal solution containing 3.8 g. (0.03 mole) of trichlorosilane[48]. Considerable heat developed during the addition. The mixture was refluxed overnight. Then the ether was distilled. The dark-gray residue was treated alternately with benzene and water. There was a

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[47] C. A. Kraus and L. S. Foster, J. Am. Chem. Soc., 49, 457 (1927).

[48] J. G. Milligan and C. A. Kraus, ibid., 72, 5297 (1950).

solid suspended between the resulting two liquid layers. The solid was separated and air-dried. There was recovered 5.7 g. (57%) of hexaphenyldigermane. The benzene layer was separated, dried and distilled. The residue was a small quantity of solid which did not melt up to 500°. None of the desired product was obtained.

Run II. The quantities of all materials used were the same as those of Run I. The modification in technique was that all contact of the reaction mixture with the atmosphere was scrupulously avoided. The sodium metal, cut into 20 pieces under an inert solvent, was attached to the reaction flask by means of a short piece of Gooch rubber tubing. The addition of the metal was thus made in the nitrogen atmosphere present over the reaction mixture. The ammonia was allowed to evaporate by having the end of an outlet tube under the surface of an inert solvent. The last traces of the ammonia were evaporated under nitrogen. The stirrer was removed before the vacuum pump step of the procedure and the system brought to atmospheric pressure with nitrogen after the pump was stopped.

There was recovered 2.4 g. (24%) of hexaphenyldigermane suspended between the two liquid layers. Separation, drying and distillation of the benzene layer gave 3.1 g. of solid melting over the range 162-190°. This product was recrystallized from a mixture of ethyl acetate and petroleum ether (b.p. 60-70°). There was isolated 1.8 g. of desired compound melting at 188-189° (*alpha*-modification). Concentration of the recrystallizing solvent afforded 0.8 g. of tris-(triphenylgermyl)-silane melting at 171-172° (*beta*-modification). The infrared spectra of these two samples are identical. The total yield was 10%.

Tris-(triphenylgermyl)-triphenylplumbylsilane (attempted)

Into the usual apparatus were placed 1.71 g. (0.00179 mole) of tris-(triphenylgermyl)-silane, 0.123 g. (0.00179 g. atom) of lithium wire (cut into pieces less than 0.5 cm. in length) and 50 ml. of anhydrous ethylamine. The solution was stirred at 0° until all the metal had reacted and a turbid, yellow solution remained. The reaction mixture was allowed to come to room temperature and the solvent evaporated under nitrogen. A total of 50 ml. of ether was added during the removal of the ethylamine. There was then added a solution of 0.55 g. (0.00179 mole) of triphenyllead chloride[49] in 50 ml. of benzene. The color of the reaction mixture changed from yellow to a deep-green during this

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[49] Kindly furnished by Dr. T. C. Wu.

addition. After 8 hours stirring at room temperature, there was noted the deposition of a black solid. The color of the solution was then amber. The mixture was hydrolyzed with 100 ml. of water. The black solid was filtered off and found to be inorganic material (Pb). The ether-benzene fraction was separated, dried and distilled. There remained a solid and a small quantity of oil. The solid, 0.97 g. (57%), was identified by the method of mixed melting points as tris-(triphenylgermyl)-silane. The oil could not be crystallized nor further identified.

Tris-(triphenylgermyl)-triphenylstannylsilane

To 50 ml. of anhydrous ethylamine at 0° were added 1.71 g. (0.00179 mole) of tris-(triphenylgermyl)-silane and 0.123 g. (0.00179 g. atom) of lithium wire cut into pieces less than 0.5 cm. in length. The solution was stirred at that temperature until all the metal had reacted and a turbid, yellow solution remained. The solvent was then allowed to evaporate at room temperature under nitrogen. An equal volume of ether was added during the ethylamine evaporation. To the resultant suspension cooled to 0°, were added 50 ml. of a benzene solution containing 1.04 g.

(0.00177 mole) of triphenyltin chloride[50]. The mixture was stirred overnight. Hydrolysis of the pale-yellow suspension with 100 ml. of water resulted in two, colorless layers. The organic layer was separated, dried and distilled. There remained a solid melting over the range 197-260° dec. and possessing an amine-like odor. This product was recrystallized from a mixture of chloroform and petroleum ether (b.p. 60-70°). There was isolated 0.36 g. of a white powder melting at 340-342° dec. Concentration of the recrystallizing solvent gave 0.74 g. of a tan solid melting over the range 140-340° dec. Further treatment of this material did not narrow the melting range. The yield of product melting at 340-342° dec. was 15.5%. It gave qualitative tests for both tin[51] and silicon-germanium[52].

Anal. Calcd. for $C_{72}H_{60}Ge_3SiSn$: Mixed oxides, 28.3; Sn[53], 9.2. Found: Mixed oxides, 28.7, 28.5; Sn, 9.0.

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[50] Kindly furnished by L. A. Gist, Jr.

[51] H. Gilman and T. N. Goreau, J. Org. Chem., 17, 1470 (1952).

[52] H. Gilman, R. K. Ingham and R. D. Gorsich, J. Am. Chem. Soc., 76, 918 (1954).

[53] E. R. Caley and M. G. Burford, Ind. Eng. Chem., Anal. Ed., 8, 114 (1936).

Organodisilanes

Pentaphenylethoxydisilane

To 20.0 g. (0.435 mole) of absolute ethanol[54] was added slowly and with stirring 2.0 g. (0.0042 mole) of pentaphenylchlorodisilane[55]. The mixture was refluxed with stirring on a water bath for one hour. At no time did complete solution take place. After cooling the reaction mixture, which was acid to litmus, a solid material was filtered off. There was obtained 1.84 g. of a white powder melting over the range 207-211°. On standing there was separated from the mother liquors 0.15 g. of material melting over the range 207-210°. Two recrystallizations of the combined solids from petroleum ether (b.p. 60-70°) gave 1.70 (83.3%) of product melting at 210.5-212°.

Anal. Calcd. for $C_{32}H_{30}OSi_2$: Si, 11.50. Found: Si, 11.35, 11.58.

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[54] Excess of alcohol was used as solvent in all cases. A product of high purity was obtained by this procedure.

[55] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, J. Am. Chem. Soc., 74, 561 (1952).

Pentaphenylbenzyloxydisilane

To 20.0 g. (0.185 mole) of benzyl alcohol[54] was added slowly and with stirring 2.0 g. (0.0042 mole) of pentaphenylchlorodisilane. The mixture was heated and complete solution resulted at 85-90°. The reaction mixture was then heated to 135° and allowed to cool slowly. There was filtered off 1.40 g. of white crystals melting over the range 164-167°. An additional 0.25 g. of crystals melting over the range 168-171° was separated from the mother liquors. Two recrystallizations of the combined solids from petroleum ether (b.p. 60-70°) yielded 1.35 g. (58.7%) of crystals melting at 170-171.5°.

Anal. Calcd. for $C_{37}H_{32}OSi_2$: Si, 10.20. Found: Si, 10.20, 10.31.

Reaction of secondary or t-butyl alcohol with pentaphenylchlorodisilane gave no alkoxydisilane derivative. Since the molar quantity of organosilicon compound is so small, a minute amount of moisture in the reagents could be responsible for the product isolated, pentaphenylhydroxydisilane. Special drying techniques[56] applied to the reagents produced no desired derivative.

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[56] L. F. Fieser, "Experiments in Organic Chemistry", 2nd ed., D. C. Heath Co., Boston, Mass., 1941, pp. 358-359.

Pentaphenylhydroxydisilane (attempted)

To 2.0 g. (0.0042 mole) of pentaphenylchlorodisilane[55] was added 95 ml. of 5% ethanolic (95%) potassium hydroxide. The mixture was refluxed over a water bath for 4 hours. More of the alcoholic hydroxide was added until the total volume was 120 ml. and complete solution resulted. After cooling, the solution was evaporated to dryness. A white, solid residue was extracted several times with hot petroleum ether (b.p. 60-70°). The remaining material was water and ether extracted. The ether layer was dried, distilled and the residue recrystallized from petroleum ether (b.p. 60-70°). From the first petroleum ether extract there was finally isolated 0.80 g. (69%) of material melting at 142.5-144°. This solid was identified as triphenylsilanol by a mixed melting point. From the ether extract there was finally obtained 0.20 g. (8.9%) of shiny crystals melting at 220-222°. This product was identified as hexaphenyldisiloxane by a mixed melting point.

The reaction using 1% ethanolic (95%) potassium hydroxide was carried out in the same manner. The same products were isolated and in similar yields.

Pentaphenylhydroxydisilane

To 20.0 ml. of dioxane was added 2.0 g. (0.0042 mole) of pentaphenylchlorodisilane[55]. On gentle warming the solid dissolved. Then 10.0 g. (0.56 mole) of distilled water was added. The solution was refluxed for 5 hours and allowed to cool. There was filtered off 1.81 g. of solids melting over the range 111.5-115°. The material was recrystallized three times from petroleum ether (b.p. 60-70°). The first yield of product was 1.62 g. (84.4%) melting at 134-134.5°. An infrared spectrogram showed a strong absorption band for the hydroxyl group.

Anal. Calcd. for $C_{30}H_{26}OSi_2$: Si, 12.17; active H, 1.00. Found: Si, 12.15, 12.30; active H, 1.06, 1.08 (Zerewitinoff).

Attempts to prepare the sym-bis-(triphenylsilyl)-tetraphenyldisiloxane proved unsuccessful. Using pentaphenylhydroxydisilane and formic acid (98-100%)[57], there was obtained a 50% recovery of the starting material. From the reaction of the sodium salt of pentaphenylhydroxydisilane and pentaphenylchlorodisilane, a glass-like substance which has thus far resisted crystallization was the only product isolated.

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[57] H. W. Melvin, Jr., Unpublished Ph.D. thesis, Iowa State College Library, 1954.

Pentaphenyldisilane

In a dry, three-necked flask fitted with Trubore glass stirrer, gas inlet tube, and a glass stopper were placed 5.0 g. (0.011 mole) of pentaphenylchlorodisilane[55] and 100 ml. of anhydrous ether. After the silicon compound had dissolved, there was added 4.0 g. (0.11 mole) of lithium aluminum hydride. The mixture was brought to reflux and kept there with constant stirring and under dry nitrogen for 18 hours. The excess lithium aluminum hydride was slowly destroyed with water and the reaction mixture acidified with 3N hydrochloric acid. The ether and water layers were separated. After the water layer had been extracted with ether several times, the combined ether fractions were dried and the solvent distilled. The white residue weighed 2.01 g. Several recrystallizations from a mixture of 95% ethanol and benzene gave 1.22 g. of shiny, flaky crystals with a melting point of 128-129°. The mother liquors gave an additional 0.25 g. of this material. The total yield of pentaphenyldisilane was 1.50 g. (32.3%). A silicon-hydrogen bond was present in the infrared spectrogram for this compound.

Anal. Calcd. for $C_{30}H_{26}Si_2$: Si, 12.67. Found: Si, 12.50, 12.60.

Hexaphenyldisilane

Method A. To 0.27 g. (0.00061 mole) of pentaphenyldisilane in 20 ml. of anhydrous ether was added 2.5 ml. (0.0021 mole) of phenyllithium. The mixture was stirred under dry nitrogen with a magnetic stirrer. Within 5 minutes, a milky solution resulted. After the solution was stirred and refluxed under dry nitrogen for 4 hours, a white precipitate settled out. As the reaction mixture was hydrolyzed with distilled water, a gas was evolved. The solid was now suspended between the ether and water layers. The material was filtered off and dried. There was obtained 0.306 g. (97.8%) of white powder melting at 361-363°. This was identified by a mixed melting point as hexaphenyldisilane.

Method B. To 0.50 g. (0.0010 mole) of pentaphenylethoxydisilane in 25 ml. of a benzene-ether (1:1) solution was quickly added 2 ml. (0.0017 mole) of phenyllithium. The solution was magnetically stirred. The reaction mixture took on a milky-white appearance in 15 minutes. After 1 hour, the suspended solids were filtered off, washed with petroleum ether (b.p. 60-70°), and air-dried. There was obtained 0.44 g. (83%) of material melting at 361-363°.

This product was identified as hexaphenyldisilane by a mixed melting point.

Organogermanium Compounds

Triphenyl-4-pentenylgermane

To a stirred suspension of 7.3 g. (0.30 g. atom) of magnesium turnings in 15 ml. of ether was added a solution of 7.45 g. (0.050 mole) of 1-bromo-4-pentene[58] in 30 ml. of ether. The reaction began immediately as evidenced by a refluxing of the suspension. After 1 hour of additional refluxing, there was obtained a 74% yield of the Grignard reagent as determined by a simple acid titration. To this 4-pentenylmagnesium bromide solution were then added 60 ml. of a mixture of benzene and ether (1:1) containing a suspension of 14.2 g. (0.037 mole) of triphenylbromogermane. There was complete solution after the completion of the addition. Color Test I was found to be positive at that time. Hydrolysis with 100 ml. of 3 N hydrochloric acid resulted in two, colorless layers. The organic fraction

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[58] H. Gilman and J. H. McGlumphy, Bull. soc. chim. France, (4) 43, 1325 (1928).

was separated, dried and distilled. There remained a solid and a liquid. The solid was separated and recrystallized from 95% ethanol. There was recovered 5.1 g. (36%) of triphenylbromogermane. The oil was treated with boiling 95% ethanol. On cooling, there precipitated 7.2 g. of "wet" solid melting over the range 35-38°. This material, on vacuum distillation, gave 6.8 g. of liquid boiling over the range 189-192° at 0.32 mm. The product solidified to give a white solid melting at 37-38°. The yield of triphenyl-4-pentenylgermane was 77.9%.

Anal. Calcd. for $C_{23}H_{24}Ge$[59]: Ge, 19.5. Found: Ge, 19.3, 19.6.

1-Triphenylgermyl-5-triphenylsilylpentane

Into the usual experimental apparatus were placed 5.0 g. (0.013 mole) of triphenyl-4-pentenylgermane, 26.0 g. (0.10 mole) of triphenylsilane, 0.30 g. (0.0013 mole) of benzoyl peroxide and 25 ml. of heptane. The mixture was heated to 85-90° and maintained with constant stirring at that temperature for 20 hours[60]. The resultant solution

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[59] C. W. Gerow, unpublished studies, Iowa State College.

[60] R. D. Gorsich, unpublished studies, Iowa State College.

was a pale-amber color. The heptane solvent was distilled at room temperature. Vacuum distillation of the remaining oil gave 21.2 g. of material boiling over the range 123-131° at 0.04 mm. and a small quantity of a highly-viscous oil. The distilled material solidified on standing and was identified by mixed melting point as triphenylsilane. The recovery was 81.5%. Treatment of the residual oil with hot 95% ethanol resulted in a tan solid melting over the range 106-118°. Several recrystallizations of this product from a mixture of 95% ethanol and ethyl acetate afforded 2.4 g. (27.3%) of desired compound melting at 137-138°.

Anal. Calcd. for $C_{41}H_{40}GeSi$: Mixed oxides, 18.9. Found: Mixed oxides, 18.7, 18.9.

Tetrakis-(p-bromophenyl)-germane (attempted)

Run I. To a stirred suspension of 10.3 g. (0.425 g. atom) of magnesium turnings in 50 ml. of ether were added 10 ml. of a solution containing 100 g. (0.424 mole) of p-dibromobenzene[46] in 300 ml. of ether. After the reaction began, as evidenced by an increasing turbidity of the reaction mixture, the remainder of the solution was added at a rate sufficient to maintain gentle reflux. Total addition time was 2 hours. Analysis by the simple acid titration method gave an 84% yield. To the Grignard reagent was then added a solution of 18.3 g. (0.085 mole) of germanium tetrachloride in 50 ml. of toluene[61]. During this addition the temperature of the reaction mixture was maintained at reflux. The ether solvent (from the preparation of p-bromophenylmagnesium bromide) was distilled (under nitrogen) and replaced by toluene. Color Test I was found to be positive after 3 more hours of reflux. The hydrolysis was carried out with 250 ml. of 3 N hydrochloric acid. A yellow solid, suspended between the aqueous and organic layers, was separated and air-dried. All attempts to recrystallize this highly-insoluble material failed. The solid, 23.1 g., softened at about 255°, but failed to melt by 500°. This material left a residue from the ignition of a small sample in the Bunsen burner. It was not further identified.

The toluene layer was separated, dried and distilled. There remained a tan oil. Vacuum distillation of this product caused the sublimation of 12.2 g. of p-dibromobenzene. The recovery was 12.2%. The residue in the distillation flask was too small to be distilled.

Run II. To 0.297 mole of n-butyllithium in 310 ml. of ether at -15° was slowly added a solution of 70.8 g. (0.30 mole) of p-dibromobenzene in 350 ml. of ether. Color Test II was negative on completion of the addition. The temperature of the solution was raised to the boiling point and the ether solvent distilled. Toluene was added to replace the ether. When all of the low-boiling solvent was replaced, a simple acid titration was carried out. There was obtained an 18% yield. The germanium tetrachloride solution was not added.

Run III. There was prepared 0.377 mole of p-bromophenylmagnesium in 350 ml. of ether by the procedure given in Run I. The ether was then distilled and replaced by toluene. Simple acid titration showed no significant change in the yield. There were then added 40 ml. of a toluene solution containing 16.1 g. (0.075 mole) of germanium tetrachloride. Considerable heat developed during the addition. The remainder of this experiment was carried out by the techniques of Run I. The results, also, were similar. None of the desired product was isolated.

Table 1

Thermal stability tests[18] on synthesized compounds

Compound	M.P.	Observations
1. Diphenyl-bis-(*p*-phenoxyphenyl)-silane	162-163	Slight volatility at 400-410°. Increasing volatility, pale amber at 475-480°. Complete volatility about 505-510°.
2. Phenyl-tris-(*p*-phenoxyphenyl)-silane	149-150	Light amber about 460°. Slight volatility about 500°. Boiling point at 530-533°; no further discoloration.
3. Tetrakis-(*p*-phenoxyphenyl)-silane	206	Melted to a pale-yellow liquid. Slight volatility about 500°. Vaporization temperature 550-560° with noticeable darkening.
4. Tris-(*p*-phenoxyphenyl)-*n*-dodecylsilane	liq. (pale-yellow)	Microbubbles from 405°. Slight volatilization about 418-420°. Boiling point around 423-425° with no further discoloration.
5. Triphenyl-*m*-trifluoromethylphenylsilane[62]	100-101	Very slight volatility at 245-250°, increasing gradually around 375-380°. Some refluxing at 385-390°. Total volatility at 400-405°, very pale-amber color.

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[62] H. Gilman, A. G. Brook and L. S. Miller, *ibid.*, *75*, 3757 (1953). The sample was prepared by L. S. Miller.

Table 1 (Continued)

Compound	M.P.	Observations
6. Diphenyl-bis-(m-trifluoromethylphenyl)-silane	96-97	Very slight volatility at 250°, increasing slightly about 320-340°. Considerable refluxing at 360°. Total volatility about 375-380° with a pale-amber color.
7. Phenyl-tris-(m-trifluoromethylphenyl)-silane	80-81	Microbubbles around 330°. Considerable volatility at 365°. Complete reflux at 370-374° with a pale-amber color.
8. Tetrakis-(m-trifluoromethylphenyl)-silane	102-103	Microbubbles and slight volatility at about 345-350°. Considerable refluxing around 360°, becoming pale amber. Total volatility at 362°, no further discoloration.
9. Triphenyl-m-tolylsilane	150-151	Very, very slight volatility around 300-310°. Pale-amber color at 375-380°. Color deepens at 395-400°. Microbubbles noted from 415°. Complete vaporization around 430°.
10. Diphenyl-bis-(m-tolyl)-silane	119-120	Very pale amber and slight volatility about 315-325°. Steadily increasing reflux from 375-410°. Color darkening and microbubbles from 422-430°. Completely volatility at 435° with a deep-amber color.

Table 1 (Continued)

Compound	M.P.	Observations
11. Phenyl-tris-(*m*-tolyl)-silane	128-129	Slight volatility around 310-320°. Pale amber at 360°. Microbubbles continuing from 380°. Complete vaporization about 420-425°.
12. Tetrakis-(*m*-tolyl)-silane	150-151	Some volatility around 295-300°. Microbubbles from 330°. Pale yellow and increased volatility about 375-380°. Completely vaporized at 435-438° with a deep-amber color.
13. Triphenyl-9-fluorenylsilane	183-184	Microbubbles above 280°. Pale yellow at 440° with some volatilization. Residue dark red by 480° and boiling point around 500°.
14. Diphenyl-bis-(9-fluorenyl)-silane	270-271	Orange at 300-305°, wine red by 330-333°. Microbubbles from 420°. Considerable refluxing at 440°. Deep red at 455-465° with noticeable decomposition.
15. Phenyl-tris-(9-fluorenyl)-silane	333-334	Melted to give a red liquid. Microbubbles from 340-360°. Slight volatility around 350-355°. Considerable darkening and refluxing at 390°. Complete vaporization and some decomposition about 410-420°.

Table 1 (Continued)

Compound	M.P.	Observations
16. Trimethyl-2-biphenylylsilane	liq.	Microbubbles noted about 260-265°. Boiling point around 270-272° with no discoloration.
17. Phenyl-tris-(*p*-trimethylsilylphenyl)-silane	189-191	Microbubbles noted at 365-370° with very slight volatility. Completely refluxing at 475-480° with a pale-yellow color.
18. Bis-(*p*,*p*'-trimethylsilyl)-diphenyl ether	liq.	Microbubbles from 355-360°. Completely refluxing at 372-373°.
19. Bis-(*p*,*p*'-triphenylsilyl)-diphenyl ether	306-307	Microbubbles from 480-485°. Slight volatility around 500°, pale-yellow color. Completely refluxing at about 557-560°.
20. Tris-(*m*-trifluoromethylphenyl)-silane	liq.	Slight volatility at 155-160°. Microbubbles from 255°. Considerable refluxing 275-280°. Boiling point about 322-325°, no discoloration.
21. Tris-(*p*-bromophenyl)-silane	107-108	Microbubbles from 355°. Slight volatility about 375-380°. Pale amber around 390-395°. Increasing volatility and becoming deep-amber at 415-420°. Complete volatility at 454-456° with considerable decomposition.

Table 1 (Continued)

Compound	M.P.	Observations
22. 1-Triphenylgermyl-5-triphenylsilylpentane	137-138	Microbubbles from 360°. Slight volatility about 380-385°. Pale-yellow around 410-415°. Considerable volatility at 425-430°. Complete volatilization at 435-437° with a deep-amber color.
23. Triphenyl-4-pentenylgermane	37-38	Slight volatility around 270-275°. Microbubbles from 295-300°. Considerable volatility at 355-360°. Boiling at 382-384°, pale yellow color.
24. Tris-(triphenylgermyl)-silane	171-172 (*beta*-modification)	Microbubbles from 347-350° becoming pale yellow. Considerable volatility around 400-405°. Complete volatility at 412-414° with no further color change.
25. Tris-(triphenylgermyl)-silane	188-189 (*alpha*-modification)	Microbubbles from 285-290°. Pale-yellow color at 360-362°. Some volatility around 387-390°, turning amber. Completely volatilized at 410-412°.
26. Tris-(*p*-trimethylsilylphenyl)-*n*-dodecylsilane	68-74 (pale-yellow)	Microbubbles around 277-280°. Some volatility around 345-350°, becoming pale amber. Complete volatilization at 390-392° without further decomposition.

DISCUSSION

Theoretical Consideration of Bond Energy and Bond Dissociation Energy Measurements

A measure of the thermal stability of an organic moiety in an organometallic molecule is the energy required to break its carbon-metal bond. This quantity of energy is defined as the bond dissociation energy. There is in general use, however, the term "bond energy" which can be related to, but is not necessarily identical with the bond dissociation energy[63]. Since both terms had a common beginning, there has been considerable confusion resulting from their non-critical, interchangeable use.

Fajans[64], who introduced the concept of bond energy, assumed that the amount of energy necessary for breaking any particular bond was "a constant magnitude, characteristic for each type of bond, and independent of the environment of the bond within the molecule"[65]. It followed, therefore, that the heat of atomization of a molecule be

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[63] G. Glockler, Ann. Rev. of Phys. Chem., 3, 151 (1952).

[64] K. Fajans, Ber., 53, 643 (1920); 55, 2826 (1922).

[65] M. Szwarc and M. G. Evans, J. Chem. Phys., 18, 618 (1950).

an additive property corresponding to the sum of all the individual bond energies. There was then evolved from the theoretical equations derived from this hypothesis a system of bond energies calculated from the heats of combustion of organic molecules.

Further development of this idea by Pauling[66] showed definitely that the assumption of constant values for bond-energies, regardless of all other organic groups present, was not acceptable. Concurrent with his work, several experimental methods[67] were devised which made it possible to calculate bond dissociation energies. It was then quickly recognized that bond energy and the dissociation energy of a bond did not have the same value.

Szwarc defines the dissociation energy of the bond X-Y in molecule (or radical) M as the "heat required to decompose M into the fragments X and Y (atoms, radicals or molecules) by rupture of only the X-Y bond."[65]

$$M = X + Y - D(X\text{-}Y) \text{ kcal./mole}$$

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[66] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N. Y., 1940.

[67] M. Szwarc, Chem. Revs., 47, 75 (1950).

The calculations must be made for the states of M, X and Y in the gaseous phase at zero pressure and 0° K. If these conditions are met, there are then calculated unambiguous values for the bond dissociation energy, D. It is also stated that the path followed for the cleavage does not affect the value found for the endothermicity of the reaction.

The concept of bond energy cannot be stated in as simple a manner. It depends critically on the value of the heat of atomization of the particles involved. There is, at this time, no commonly accepted figure for this value for carbon. Springall defines the heat of atomization as the "enthalpy change ($\triangle H$) present in the transformation of 1 g. atom of carbon (graphite form) to the free ground state (^3P) atoms"[68]. The symbol L represents the latent heat of sublimation for the graphite transformation at 0° K. This energy term is directly involved in all applications of molecular structural ideas to thermochemical data in organic chemistry. A great number of experiments, mainly from spectroscopic data (especially for carbon monoxide) and thermodynamic and kinetic data, have resulted in several values for the L of carbon. These were all accurately

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[68] H. D. Springall, <u>Research</u>, <u>3</u>, 260 (1950).

determined and have reliable investigators as proponents for each. Values are 170.4, 141.2, 136.1 and 125.0 kcal./g. atom. Since an unequivocal evaluation has not yet been obtained, there must be a measure of doubt associated with all bond energy calculations.

There is likewise considerable controversy about the value for silicon. The figure used by Pauling was obtained by a doubtful direct measurement[69]. Gilman and Dunn[5] use a number twice that calculated for the dissociation energy of the silicon-silicon bond from the thermal decomposition of disilane[70].

The use of these various L values forbids the direct comparison of many published data even for obtaining differences in orders of magnitude for these energies. Another problem involves the final state of the particles in the atomization process. In the dissociation energy case, there is an increase from one to two particles on which the final state measurement must be made. In a polyatomic molecule of even comparative simplicity, the measurement problems at complete atomization are apparent. More difficulties and

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[69] F. R. Bichowski and F. D. Rossini, "The Thermochemistry of the Chemical Substances", Reinhold Publishing Corp., New York, N. Y., (1936).

[70] H. A. Skinner, _Trans. Faraday Soc._, _41_, 645 (1945).

ambiguities are encountered when the attempt is made to distribute the heat of atomization between the various bonds in the molecule. Compounds with one type of bond, such as CH_4, are easily handled, with the total bond energy being four times that of one C-H linkage. Much remains to be done with molecules containing several types of bonds. From the above statements, it can be seen that both ambiguous definitions and uncertain physical constants contribute to the slow progress of theoretical and practical evaluations in the field of thermal stability.

Helm and Mack[71], from a kinetic study of the thermal decomposition of tetramethylsilane, have calculated a value of 78.8 kcal./mole for the energy required to break the first silicon-methyl bond. In an extension of these studies, Waring[72] determined the dissociation energy for the first carbon-silicon bonds in tetraethyl- and tetra-n-propylsilane. The values found were 50.5 and 46 kcal./mole respectively. The author points out that he is uncertain as to whether to attribute this difference to the negative influence of the additional methyl group, or to slight variation in the two reaction mechanisms. He postulates the following

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[71] D. F. Helm and E. J. Mack, J. Am. Chem. Soc., 59, 60 (1937).

[72] C. E. Waring, Trans. Faraday Soc., 36, 1142 (1940).

mechanism for tetraethylsilane from kinetic data and chemical analysis of the products:

$$\text{Primary process}\quad \mathrm{Si(C_2H_5)_4} = \mathrm{Si} + 4\dot{\mathrm{C}}\mathrm{_2H_5}\ ,$$

$$\text{or}\quad \mathrm{Si(C_2H_5)_4} = \dot{\mathrm{S}}\mathrm{i(C_2H_5)_3} + \dot{\mathrm{C}}\mathrm{_2H_5}\ \text{(slow)},$$

$$\dot{\mathrm{S}}\mathrm{i(C_2H_5)_3} = \mathrm{Si} + 3\dot{\mathrm{C}}\mathrm{_2H_5}\ .$$

$$\text{Secondary process}\quad \dot{\mathrm{C}}\mathrm{_2H_5} = \mathrm{C_2H_4} + \dot{\mathrm{H}}\ ,$$

$$2\dot{\mathrm{H}} = \mathrm{H_2}\ \text{(fast)}\ ,$$

$$\mathrm{C_2H_4} = \mathrm{C} + \mathrm{CH_4}\ .$$

For the tetra-n-propylsilane, the primary process is analogous, but the secondary process is thought to be:

$$\text{Secondary process}\quad \dot{\mathrm{C}}\mathrm{_3H_7} = \mathrm{C_3H_6} + \dot{\mathrm{H}}\ ,$$

$$2\dot{\mathrm{H}} = \mathrm{H_2}\ \text{(fast)}\ ,$$

$$\mathrm{C_3H_6} + 2\dot{\mathrm{H}} = \mathrm{C_2H_4} + \mathrm{CH_4}\ ,$$

$$\mathrm{C_2H_4} = \mathrm{C} + \mathrm{CH_4}\ .$$

By carrying out the reaction in the presence of nitrogen(II) oxide, he formulated the free radical mechanism and claimed that the decomposition involved no chain reactions.

All three authors indicate that the carbon-silicon bond is the first bond to be cleaved. Calculations on Pauling's scale, previously mentioned, resulted in essentially equal values for the carbon-carbon and carbon-silicon bond energies. The identical evaluations made by Gilman and Dunn[5] from Skinner's work lead to the conclusion that the carbon-silicon bond is definitely weaker. The latter fact is in agreement with experimental results just described.

In an another attempt to determine which of the values for the heat of atomization of silicon was correct, a study was carried out on the heats of formation and combustion of some organosilicon compounds[73]. All the molecules contained at least two silicon-oxygen bonds. There was good agreement between the observed and calculated (Pauling's data) values for the heat of formation of hexamethylcyclotrisiloxane. Values for hexaphenylcyclotrisiloxane, diethylsilandiol, dimethyldiethoxysilane and di-*n*-propyldiethoxysilane varied from 23.5 to 93.4 kcal./mole from the observed values. Gilman and Dunn[5], using their revised data for the silicon heat of atomization, obtain good agreement for the dimethyl-

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[73] T. Tanaka, U. Takahashi, R. Okwara and T. Watasi, *J. Chem. Phys.*, *19*, 1330 (1951).

and dihydroxysilanes. However, there is a poor correlation for both the first and last compounds studied.

Some work has been done with the dissociation energies of carbon-germanium, -tin and -lead bonds. Geddes and Mack[74] give the value of 51 kcal./mole as the dissociation energy for the decomposition of gaseous tetraethylgermane. There is a good indication from the types of carbon-containing products obtained, that some energy was used in the breaking of carbon-carbon as well as germanium-carbon bonds. This would mean a lower value for the dissociation energy of the latter linkage. For the carbon-tin bonds, Long and Norrish[75] report a total dissociation energy of 195.9 kcal./mole. If the division by four accurately gives the value for the cleavage of the initial carbon-tin linkage, the figure would be 49 kcal./mole. The authors also readily point out that some doubt still exists about the constant for the heat of atomization of the metal. A kinetic study on the decomposition of gaseous tetraethyllead was carried out by Leemakers[76]. He reports the energy for the "decomposition"

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[74] R. L. Geddes and E. Mack, J. Am. Chem. Soc., 52, 4372 (1930).

[75] L. H. Long and R. G. W. Norrish, Trans. Roy. Soc., A 241, 587 (1949).

[76] J. A. Leemakers, J. Am. Chem. Soc., 55, 4508 (1933).

to be 36.9 kcal./mole. No definite statement is made as to whether this value is to be construed as that required to break the first carbon-lead bond.

It should be pointed out that the germanium and lead studies antedate the clarification between bond energy and bond dissociation energy as formulated by Pauling.

An investigation into the theoretical basis for the thermal stability of organic radicals was made by Szwarc[77]. He ascribed the difference in chemical behavior of these species to their generally low thermal stability and high reactivity compared to molecules and ions. The lowered thermal resistance was due to a considerable decrease in the dissociation energy of some of their bonds. Considering the reaction,

$$\dot{C}H_2\text{-}CH_2\text{-}H \quad = \quad CH_2{=}CH_2 + \dot{H} \;,$$

the author states that simultaneously with the breaking of the C-H bond, there is formed "the other half" of double bond of ethylene. The energy liberated in this formation thus reduces the endothermicity required from an outside source for the C-H bond cleavage. The bond dissociation

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[77] M. Szwarc, Discussions Farad. Soc., 10, 143 (1951).

energy for the ethyl radical is, therefore, lower than that for ethane by the quantity needed to complete double bond formation. The claim is also made that the bond dissociation energy and concomitantly, the thermal stability is increased through resonance stabilization. For the sake of accuracy, he points out that thermal stability is not measured by the dissociation energy, but by the activation energy of the dissociation process. This energy is larger than that of bond dissociation by the activation energy of the addition process

$$\text{olefin} + \text{R} = \text{olefin-R} .$$

If R equals methyl or hydrogen, the value of the extra energy is so small that it does not change the comparative thermal resistance of radicals as calculated from bond dissociation energy.

Szwarc postulates that molecules incapable of double bond formation should be expected to possess higher thermal resistivity than those forming the unsaturated linkage. For that reason, the benzyl radical would be more stable than the allyl radical, even though the resonance stabilization of the latter would be higher. He expects other radicals of this type, such as phenyl, diphenylmethyl, betanaphthylmethyl and triphenylmethyl to have rather high thermal resistance.

Organosilicon Compounds

Melting point relationships

In addition to the problem of finding organic groups capable of imparting high thermal stability to a molecule, there was the concomitant problem of having this same compound possess a rather low melting point. Actually, the most desirable materials were to be liquids at room temperatures. It was soon very evident from the concurrent studies[18] in This Laboratory that the promising compounds must be unsymmetrical types. These molecules, in general, had the lower melting points. In the series diphenyl-bis-(p-phenoxyphenyl)-, phenyl-tris-(p-phenoxyphenyl)- and tetrakis-(p-phenoxyphenyl)-silane the melting points are 161-162°, 149-150° and 204°. For the corresponding compounds having the m-trifluoromethylphenyl group replacing the p-phenoxyphenyl, the respective melting points are 97-98°, 80.5-81° and 102-103°. In both groups, the phenyl-tris-substituted molecules possessed melting points 10-15° lower than those of compounds having more symmetrical structures. This was not the case, however, for the m-tolyl series. In the four compounds synthesized there was a decrease in the melting point from triphenyl-m-tolylsilane, m.p. 150-151°, to diphenyl-bis-(m-tolyl)-silane, m.p. 119-120°, and then a steady increase as the number of m-tolyl groups was increased. Phenyl-tris-(m-tolyl)- and tetrakis-(m-tolyl)-silane had melting points of 128-129° and 150-151°, respectively. For the 9-fluorenyl-containing molecules there was a continuous increase in the melting points for the synthesized compounds. Triphenyl-9-fluorenyl-, diphenyl-bis-(9-fluorenyl)- and phenyl-tris-(9-fluorenyl)-silane had melting points of 183-184°, 270-271° and 333-334°, respectively. The tetrakis-9-fluorenyl-molecule could not be made. In order to more accurately visualize the possible steric hindrance present in the latter compound, a Fischer-Hirschfelder-Taylor model was attempted. It was not possible to form the fluorenyl nucleus. A model of the related diphenylmethyl system indicated that steric factors may considerably hinder the formation of the desired compound.

It is to be noted that with the exception phenyl-tris-(m-trifluoromethylphenyl)-silane, m.p. 80.5-81°, all the compounds described above melt at or over 100°. Thus, it became evident that at least one unit of a group known to give low melting point properties had to be incorporated into these molecules to meet the low melting point requirement of the problem.

Volatilization temperature relationships

The volatilization temperature ranges of the synthesized series of compounds ranged from a low of 362° for tetrakis-(m-trifluoromethylphenyl)-silane to a high of 550-560° for tetrakis-(p-phenoxyphenyl)-silane. It is interesting to note that both the lowest and highest boiling molecules are fully-symmetrical, tetra-substituted compounds. All members of the m-trifluoromethylphenyl-substituted series had volatilization temperatures in the range 362-380°. The boiling points for the four members in order of increasing number of fluorinated-substituents are 400-405°, 375-380°, 370-374° and 362°, respectively. This is a continuous lowering of the volatilization temperature with an increase in molecular weight. In the m-tolyl series there was found a nearly constant range of boiling points. The values for the molecules from the triphenyl-m-tolyl- through the tetrakis-m-tolylsilane are 430°, 435°, 422-425° and 435-438°, respectively. Thus it can be seen that replacement of fluorine atoms by hydrogen in the trifluoromethyl group on the benzene ring leads to a considerable increase in the volatilization temperatures.

The phenyl-9-fluorenyl-silane compounds have steadily decreasing boiling points as the number of 9-fluorenyl groups is increased. This trend is similar to that of the m-trifluoromethylphenyl series, but the lowering between successive members is much more pronounced. Triphenyl-9-fluorenylsilane is completely volatilized at 500°, diphenyl-bis-(9-fluorenyl)-silane about 455-465° and phenyl-tris-(9-fluorenyl)-silane at 410-420°. The difference in boiling point between the first and third compound is 80-90°. The analogous lowering in the m-trifluoromethylphenyl-containing molecules is 25-30°. It must be pointed out that all the 9-fluorenyl compounds were red liquids and suffered noticeable decomposition near their vaporization points. There is considerable reason to believe, therefore, that the volatilization temperatures noted were not of the pure compounds, but of some decomposition products.

Another pattern in boiling point variation was discovered in the phenyl-p-phenoxyphenyl-silane group. There was a continuous increase in volatilization temperatures with an increase in the molecular weight. The boiling points given in order of increasing number of p-phenoxyphenyl groups are, 475-480°, 530-533° and 550-560°. The introduction of this group into the molecules gave the compounds with the highest volatilization temperatures.

Thermal stability relationships

The criterion used to determine the degree of decomposition of the tested compounds was the amount of discoloration of the material with increasing temperature. The series showing this phenomenon closest to the melting points of the individual members was that containing the 9-fluorenyl group. Triphenyl-9-fluorenylsilane, m.p. 183-184°, became pale yellow at 440° and dark red by 480°. The diphenyl-bis-(9-fluorenyl)-silane was orange at 300-305°, only 30° above the melting point. The tris-9-fluorenyl-substituted molecule melted at 333-334° to give a red liquid. All three compounds finally volatilized after considerable decomposition. Another group suffering noticeable darkening below the volatilization temperatures was the m-tolyl. Although a pale-yellow color was not visible until an average of 220-240° above the melting points, the deep-amber appearance at the vaporization temperatures gave evidence of considerable decomposition. The m-trifluoromethylphenyl-containing molecules possess undesirably low boiling points but have the advantage of little discoloration at these temperatures.

None of the four compounds of this series listed in Table 1 became darker than pale amber from room temperature to the vicinity of 360-370°. The group capable of withstanding the highest heat intensity is the p-phenoxyphenyl. With the exception of tetrakis-(p-phenoxyphenyl)-silane, which melted to a pale-yellow liquid, the members of this series did not show any signs of decomposition until about 460°. This is approximately 100° higher than the m-trifluoromethylphenyl compounds. The diphenyl-bis-(p-phenoxyphenyl)- and phenyl-tris-(p-phenoxyphenyl)-silane volatilized in the 505-535° range without further discoloration. The tetra-substituted molecule, though boiling at 550-560°, showed signs of darkening in that temperature range. It can thus be stated that the latter series was the most promising toward meeting the thermal stability requirements of the problem.

The formation of microbubbles well below the boiling points of most of the compounds listed in Table 1 has lead to speculation concerning their significance. C. P. Haber[78] has noticed this phenomenon in related work with polymers at high temperatures. He reports that on cooling a sample which has been heated enough to evolve these bubbles there

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[78] C. P. Haber, U. S. Naval Ordnance Laboratory, Corona, California, in private communication of April 18, 1955 to Dr. Henry Gilman.

is no apparent change in the physical properties of the polymer tested. Yet, he can find no plausible explanation for this effect other than an indication of decomposition. The melting point of some compounds from Table 1 (especially those which did not appreciably darken during the thermal stability tests) were retaken after evolution of the microbubbles. No changes in this physical constant were noted. In addition, deterioration, as evidenced by discoloration of the tested samples, did not necessarily coincide with the formation of the bubbles. Many samples were colorless at their vaporization temperatures although microbubbles were evolved. The evidence at this time seems to indicate that gases, trapped during the melting of solid compounds or distillation of liquid samples, may be responsible for this phenomenon.

Synthetic problems

The p-trimethylsilylphenyl-group was found by other workers[18] in This Laboratory to impart rather high thermal stability to a molecule, yet give materials with low melting points. The tris-(p-trimethylphenyl)-silane was prepared. It was planned to react this material with organolithium reagents[79] prepared from groups having known thermal resistivity. The desired R_3SiR' compounds could not be prepared. At first the low solubility of the silicon-hydrogen bonded molecule in ether was held responsible for the failure to effect the desired reaction. The use of benzene solutions did not alter the lack of reactivity. The possibility that electrical effects may retard reaction seems unlikely from the findings of Roberts, McElhill and Armstrong[80]. They showed that the electron-releasing ability of the p-trimethylsilyl group is of an inductive nature and should not impart any appreciable negative character to the silicon atom bonded to the hydrogen. A sample of tris-(p-trimethylsilylphenyl)-silane made by Fischer-Hirschfelder-Taylor models substantiated the thought that steric factors prevented the desired reactions. The same factor may be responsible for the absence of any interaction between tris-(m-trifluoromethylphenyl)-silane and organolithium reagents. Since even the preparation of tris-(p-phenoxyphenyl)-silane failed, this entire approach to the synthesis

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[79] H. Gilman and R. N. Clark, J. Am. Chem. Soc., 69, 1499 (1947); H. Gilman and H. W. Melvin, Jr., ibid., 71, 4050 (1949).

[80] J. D. Roberts, E. A. McElhill and R. Armstrong, ibid., 71, 2923 (1949).

of a promising series of unsymmetrical organosilicon compounds was unsuccessful.

Suggestions for Further Research

Since organic groups imparting thermal stability to a molecule in the vicinity of 500° have been found, the problem of undesirably high melting points must be studied. The groups most promising in their ability to provide a low melting point without the associated great decrease in thermal stability are of the long-chained, n-alkyl types. When the number of carbons in the chain was from eleven to eighteen, one such moiety in a molecule brought the melting point well below 100° and, in many cases, well below room temperature. The preparation of a series of triaryl-n-C_{11}-C_{18} alkyl-silanes should be carried out. The synthetic problems involved are of such a nature that mixtures are often obtained. Add to this the high boiling points and high viscosity of the desired compounds, and the need for a rather complex distillation apparatus becomes evident. With such equipment, the synthesis of molecules of the type $R_2R'SiC_{11}$-C_{18}-n could be considered. Materials of this nature could be custom-made from groups giving thermal resistivity over varying temperature ranges.

Another possible area for investigation has been opened with the synthesis of the silicon analog of 9,9-diphenylfluorene. The introduction of silicon into the fluorene system has led to the formation of a cyclic system with silicon as the hetero atom. More molecules of this type should certainly be prepared and investigated to determine their resistance to high temperatures.

The comparison between organosilicon and -germanium compounds in regard to their thermal stability is by no means complete. The small number of commercially available, germanium-containing, starting compounds has hindered the work. Attempts should be made to prepare more germanium analogs of promising molecules in the silicon series. The preparation of organic compounds containing both germanium and silicon has produced molecules with considerable thermal resistance. This approach to the stability problem may prove to be of interest.

SUMMARY

A survey of the literature on the pyrolysis and thermal stability of organosilicon and some organolead compounds was made.

An abstract of a long-term study in progress on the thermal stability of various organometallic compounds was made through May, 1955.

There were synthesized several series of organosilicon molecules of the type triphenylmonoaryl- through tetraarylsilane. The aryl groups were p-phenoxyphenyl, m-trifluoromethylphenyl and m-tolyl. A similar series containing the 9-fluorenyl group was also prepared. In only the m-tolyl series were all four compounds made.

Table 1 listing the results of thermal stability studies on the synthesized molecules was prepared.

Tris-(triphenylgermyl)-triphenylstannylsilane, a molecule having four Group IVB elements bonded to each other was synthesized in 15% yield.

Some reactions of pentaphenylchlorodisilane were studied to compare them with those of analogous monosilanes.

Some organogermanium and organosilicon-germanium compounds were prepared and tested for thermal stability.

An attempt was made to distinguish between bond energy and bond dissociation energy as related to the theoretical basis for thermal stability studies.

ACKNOWLEDGMENT

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