Hence the bromination of triphenylbenzylstannane results in the removal of phenyl groups, the reaction proceeding according to the equation $(C_6H_5)_3$-$(C_6H_5CH_2)Sn + 2Br_2 = (C_6H_5)(C_6H_5CH_2)SnBr_2 + 2C_6H_5Br$.

The author wishes to acknowledge his indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which assisted in defraying the expenses of the present investigation.

Summary

1. It has been shown that on bromination of triphenylbenzylstannane the phenyl groups are first removed.

2. The series arrangement of some organic groups based on the relative ease of removal from tin by halogen is: phenyl, benzyl, methyl, ethyl, propyl.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE CONSTITUTION OF TRIPHENYLSILICANE AND ITS REACTION WITH SODIUM IN LIQUID AMMONIA[1]

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The present study was undertaken as a part of a broader investigation now in progress in this Laboratory, which deals with certain of the fundamental properties of the element silicon in its organic combinations. In attacking this problem it was necessary to form organic silicon derivatives of the general type R_3SiNa to be used as reagents. Since the corresponding halides R_3SiX are completely ammonolyzed by liquid ammonia, it was attempted to prepare the desired compound by the action of sodium on triphenylsilicane in the same solvent. The corresponding reaction of sodium with triphenylstannane takes place readily and quantitatively. When, however, this simple reaction was attempted in the case of the silicane, unexpected results were obtained and it was found necessary to carry out a detailed study, the results of which are described in the present paper.

Ladenburg[3] reports the preparation of triphenylsilicane, melting at 200–203°, by the action of sodium and a little benzene upon triphenyl silicon bromide. On the face of it, this reaction seems a little improbable, especially in view of the fact that the corresponding triphenylstannane, and triphenylgermane, recently prepared, have been found to melt at

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[1] This paper is constructed from a portion of the Dissertation presented by Harry H. Reynolds to the Faculty of the Graduate School of Brown University, in June, 1928, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Rice Fellow, 1925–1926; Metcalf Fellow, 1926–1927.

[3] Ladenburg *Ber.*, **40**, 2278 (1907).

about 25°[4] and 47°,[5] respectively. Our work has shown that the earlier results of Ladenburg are in error, and that the compound of the formula $(C_6H_5)_3SiH$ melts at 36°.[6]

The silicane, which is a white crystalline solid, was first synthesized by Nelson,[7] who treated silicochloroform with phenylmagnesium bromide. The reaction takes place according to the equation $SiHCl_3 + 3C_6H_5MgBr \longrightarrow SiH(C_6H_5)_3 + 3MgBrCl$. He analyzed the silicane for silicon but did not examine it further. The present writers have confirmed the synthesis and fully established the constitution of the compound in the following manner. (1) The molecular weight of the material was determined and found to correspond to the formula requirements; (2) the substance was quantitatively brominated and one mole of hydrogen bromide was evolved for each mole of the silicane used, and (3) the triphenyl silicon bromide formed in (2) yielded, upon hydrolysis, an approximately quantitative amount of pure, known triphenylsilicol, $(C_6H_5)_3SiOH$.

When triphenylsilicane is treated with sodium in liquid ammonia solution, a very simple reaction might be expected to take place, namely, $(C_6H_5)_3SiH + Na \longrightarrow (C_6H_5)_3SiNa + {}^1/_2 H_2$, which calls for the utilization of 1 gram atom of sodium and the evolution of $^1/_2$ mole of hydrogen per mole of the silicane employed. Actually, however, only $^2/_3$ gram-atom of sodium was consumed and 1.9 atoms of hydrogen were evolved in the reaction. Furthermore, since a distinct end-point was reached, the excess of hydrogen could not have come from any interaction between the sodium and the ammonia. If the above reaction occurred, the addition of ammonium bromide to the solution should regenerate the original material, according to the equation $(C_6H_5)_3SiNa + NH_4Br \longrightarrow (C_6H_5)_3SiH + NaBr + NH_3$. Actually, the product obtained under these conditions, upon evaporation of the liquid ammonia, consisted of a white crystalline solid melting at 175° and a thick sirup which was not further investigated. About two-thirds of the original silicon was recovered as crystalline solid. The addition of reagents other than ammonium bromide, such as ethyl or phenyl bromide or oxygen, yielded, in every case, the same crystalline product.

[4] L. S. Foster, "Thesis," Clark University, **1923**.

[5] Kraus and Foster, This Journal, **49**, 465 (1927).

[6] Since the above was written an article has appeared by Kipping and Murray, *J. Chem. Soc.*, **131**, 360 (1929), in which they have prepared a substance believed to be triphenylsilicane, as a by-product in the destructive distillation of octaphenylcyclosilicotetrane under reduced pressure. They describe it as an oil which did not solidify at 0°. Analyses, molecular weight determination and hydrogen equivalent, corresponding closely to the values required by the formula $(C_6H_5)_3SiH$ are given, as well as certain reactions tending to confirm the constitution of the product. It seems certain that these investigators had in hand a somewhat impure sample of the silicane, as it failed to solidify at 0°.

[7] Walter K. Nelson, unpublished work, **1927**.

The substance melting at 175° is very stable, not being affected by the air or even by boiling dilute sodium hydroxide. It is rather difficultly soluble in alcohol and crystallizes well from this solvent. When analyzed for silicon it gave figures closely corresponding to the values required for triphenylsilicon or hexaphenylsilico-ethane, while molecular weight determinations yielded values closely approximating those required by the formula $[(C_6H_5)_3Si]_2$ or hexaphenylsilico-ethane. However, this latter compound has previously been synthesized and melts at 354°.[8] We have prepared a sample of this silico-ethane by the method described in the literature and have shown that our substance is structurally different, inasmuch as no transition from one into the other occurred when they were melted together.

The material melting at 175° was brominated in carbon tetrachloride in an effort to throw light upon its constitution. One-half of the silicon appeared as triphenyl silicon bromide, while all the rest of the bromine employed went to form bromobenzene. A very small quantity of di-triphenyl silicon oxide was also isolated. The remainder of the material produced in the bromination consisted of pasty by-products which were not further examined. No definite conclusions could be drawn from these experiments.

At this point it was discovered that the substance melting at 175° could be hydrolyzed readily by means of hydrochloric acid, and that the inorganic product of hydrolysis was ammonium chloride. Inasmuch as our material was quantitatively stable toward boiling alkali, and since all compounds containing a silicon–nitrogen linkage, with which we were familiar, hydrolyzed even in moist air, this observation was entirely unexpected. However, it was established that the material contained 2.6% of nitrogen, which corresponds closely to that required by di-triphenylsilicon-imine, $[(C_6H_5)_3Si]_2NH$. The analytical results above described correspond, within the normal limits of error, to the values required by this formula, while the amount of hydrogen evolved in the preparation, as well as the phenomena observed in the bromination, may also be accounted for. Finally, the product of hydrolysis of the imine, other than ammonium chloride, which should be triphenylsilicol, has been identified as such.

A somewhat similar reaction has been observed in this Laboratory by Eatough,[9] who treated triphenylsilicane with lithium dissolved in ethyl amine. In this case, also, $^2/_3$ gram-atom of the metal reacted with 1 mole of the silicane and 1 mole of hydrogen was evolved, but the products were not further investigated. The mechanism of these reactions is as yet obscure, though undoubtedly complex.

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[8] Schlenk, Renning and Racky, *Ber.*, **44**, 1178 (1911).

[9] Harry Eatough, unpublished work, **1928**.

Altogether, the structure of the substance melting at 175° seems definitely established as di-triphenylsilicon-imine, notwithstanding its extraordinary stability in alkaline solution, not frequently observed in compounds of this type.

Experimental

Triphenylsilicane.—This compound was prepared according to the method of Nelson[7] as follows. A Grignard reagent was prepared in the usual manner from 185 g. of bromobenzene, 28.6 g. of magnesium and 400 cc. of anhydrous ether. This solution (4.5 molar equivalents) was cooled to 0° and 36.2 g. of silicochloroform dissolved in 200 cc. of anhydrous ether was slowly added to it. After standing at room temperature for two hours the mixture was boiled for twenty hours. The resulting crystalline mass was cooled to 0°, acidified with dilute sulfuric acid, extracted with ether and the solvent distilled. The residue was fractionated twice at 2 mm. and the final product collected from 152–167°. It condensed as a colorless oil which on cooling solidified to a white solid; yield, 52 g. or 73% of the theoretical. Upon recrystallization from 95% alcohol, under 21°, white plates were formed melting at 36–37°. At higher temperatures the compound separated as an oil.

Anal. (Nelson) Subs., 0.3716, 0.3580, 0.4880: SiO_2, 0.0852, 0.0830, 0.1131. Calcd. for $C_{18}H_{16}Si$: Si, 10.78. Found: Si, 10.71, 10.83, 10.83.

Mol. wt. Subs., 0.1941, 0.1930, 0.1941: Benzene, 21.79, 21.77, 21.77; ΔT, 0.177°, 0.173°, 0.179°. Calcd. for $C_{18}H_{16}Si$: 260. Found: 252, 256, 249.

Bromination of Triphenylsilicane in Carbon Tetrachloride Solution.—In this experiment an all glass apparatus was used, arranged in such a manner that a current of nitrogen could be passed through the reacting mixture and the gases produced (N_2, HBr and CCl_4 vapor) conducted through a reflux condenser and then an absorption train. This consisted of a trap containing metallic mercury to absorb free bromine, a U-tube immersed in liquid ammonia to condense any carbon tetrachloride vapor and finally a series of bulbs partly filled with 10% sodium hydroxide solution to absorb all the hydrobromic acid evolved. One mole of triphenylsilicane was placed in this apparatus and 1 mole of bromine dissolved in carbon tetrachloride added through a side tube. The mixture was allowed to stand for some time to complete the reaction and the carbon tetrachloride was then frozen by means of a liquid ammonia bath to liberate the dissolved hydrobromic acid. A current of dry nitrogen was now passed through the solidified mass to carry all the hydrobromic acid into the absorption train. In the course of an hour the mixture was allowed to warm up and was finally boiled to expel the last traces of hydrobromic acid. The sodium hydroxide solution was carefully washed out of the bulbs, acidified with nitric acid and the bromine precipitated as silver bromide in the usual manner.

Anal. Subs., 1.000: Br, 0.614; AgBr, 0.724. Mols HBr/mole subs.: 1.00.

Upon hydrolysis of the brominated product formed in the reaction by boiling with dilute sodium hydroxide solution, a 93% yield of practically pure triphenylsilicol (m. p. 148–151°) was obtained.

Reaction between Triphenylsilicane and Sodium in Liquid Ammonia.—To a suspension of triphenylsilicane in anhydrous ammonia there was added, in small portions, one mole of metallic sodium. As the metal was added, a moderately vigorous reaction occurred, accompanied by the appearance of a deep red color and the copious evolution of an inflammable gas, later identified as hydrogen. As the reaction progressed the silicane gradually dissolved and a colorless crystalline product separated. When approximately two-thirds of the sodium had been added, the evolution of gas ceased and a permanent blue color, due to an excess of the metal, was imparted to the solution. Further additions of sodium produced no further apparent change. Ammonium bromide was then added, in small portions, to the mixture. The blue color was first discharged and the red color gradually faded, with the momentary formation of a white curdy precipitate. The color finally disappeared entirely, and from then on until one mole of ammonium bromide had been added, a white curdy precipitate continued to be formed. When the reaction was complete, the liquid ammonia was allowed to evaporate and the reaction mixture was extracted with carbon tetrachloride. The solvent was removed by distillation and a white solid mass remained which, upon recrystallization from 95% alcohol, yielded a white crystalline product melting at 170–175°. Approximately two-thirds of the product consisted of this substance and the remainder, recovered by evaporating the alcoholic mother liquor, was a thick sirup, from which no single substance could be isolated. Further crystallization of the solid from alcohol yielded long white needles melting at 175°.

It was especially noteworthy, in the above reaction, that the addition of ethyl bromide, phenyl bromide or oxygen, instead of ammonium bromide, yielded in every case the same crystalline product, m. p. 175°. This indicated that the substance was formed directly by the action of the sodium with the triphenylsilicane, and not later upon the addition of ammonium bromide.

Anal. Subs., 0.3008, 0.3002, 0.3901: SiO_2, 0.0683, 0.0692, 0.0896. Subs., 0.3808, 0.5101: 16.58, 14.39 cc. of 0.1008 *N* NaOH; 20.04, 20.18 cc. of 0.1199 *N* HCl; blank, 0.23 cc. of HCl. Calcd. for $C_{36}H_{31}Si_2N$: Si, 10.61; N, 2.62. Found: Si, 10.66, 10.82, 10.78; N, 2.59, 2.58.

Mol. wt. Subs., 0.3866, 0.3807: benzene, 21.78, 21.78; ΔT, 0.174°, 0.167°. Calcd. for $C_{36}H_{31}Si_2N$: 534. Found: 510, 524.

The analysis for silicon was carried out by treating the sample in a pyrex test-tube with fuming sulfuric acid and then with successive portions of fuming nitric acid until decomposition was complete. The acids were evaporated and the residue of silicon dioxide was ignited and weighed.

The analysis for nitrogen was conducted in the following manner. The sample was boiled for half an hour with 6 *N* hydrochloric acid, the mixture filtered and the residue washed free from chlorides. The filtrate was evaporated to a small volume, poured into a Kjeldahl apparatus, made alkaline and the ammonia collected in the usual manner in standard hydrochloric acid. The residue from the filtration, on crystallization from petroleum ether, melted at 151–152°. A known sample of triphenylsilicol, $(C_6H_5)_3SiOH$, and a mixture of the two each melted at the same point.

Quantitative Determination of the Gas Evolved in the Reaction between Triphenylsilicane and Sodium in Liquid Ammonia.—The treatment of the silicane with the sodium was carried out in an apparatus arranged in such a manner that all of the gas evolved might be collected over water, to dissolve most of the ammonia. The gas was then drawn very slowly through a drying tube containing phosphorus pentoxide into an evacuated bulb of known weight and volume. A manometer was attached to the system and the volume of the drying tube and connecting tubes was known. The molecular weight of the gas was calculated from the weight, pressure and temperature of the gas in the density bulb, together with the known volume of the bulb. The total volume of the gas at N.T.P. was determined in a similar manner from its pressure, temperature and the known volume of the entire containing system. The molecular weight obtained indicated that the gas must be hydrogen, and a correction to the total volume of hydrogen was calculated, upon the assumption that the only impurity in it was ammonia. The results of this experiment are indicated below.

Mol. wt. Gas in bulb, 0.0115, 0.0156 g.; *P*, 200, 212 mm.; *T*, 25°, 27°; vol. of bulb, 351.4 cc. Calcd. for H_2: 2.0. Found: 3.1, 3.9. *Total vol. of gas.* Subs., 1.086, 1.029; Na, 0.096, 0.091; *P*, 200, 212 mm.; *T*, 25°, 27°; vol. of system, 391 cc.; vol. of pure H at N.T.P., corr. for NH_3 content, 87.0, 86.4 cc. Gram atoms of H_2 per mole of $(C_6H_5)_3SiH$, 1.8, 1.9.

Summary

1. The constitution of triphenylsilicane, melting at 36°, has been established.

2. The reaction between triphenylsilicane and sodium in liquid ammonia has been studied. The chief product of the reaction was found to be di-triphenylsilicon-imine, $[(C_6H_5)_3Si]_2NH$.

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[CONTRIBUTION FROM THE DENVER STATION, FOOD, DRUG AND INSECTICIDE ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

MONOBROMOGUAIACOL CARBONATE. ESTIMATION OF GUAIACOL CARBONATE

BY LEWIS H. CHERNOFF

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As far as the writer is aware there are only two published methods for the estimation of guaiacol carbonate. One method[1] depends on the solubility of the carbonate in ether and its use is therefore limited to mixtures which do not contain other ether-soluble substances. In the other[2] the substance is saponified with alcoholic potassium hydroxide, acidified and after the addition of sodium chloride the volume of guaiacol is read.

The method herein described is more specific and depends on the conversion of guaiacol carbonate into a bromine derivative insoluble in 50% methyl alcohol.

When bromine is added to a solution of guaiacol carbonate in methyl alcohol, large needle-like crystals begin to separate out almost immediately. The compound is reasonably pure and after recrystallization from hot 95% ethyl alcohol melts sharply to an oil at 178°. It is easily soluble in chloroform, ether, benzene and hot methyl and ethyl alcohols, but less easily soluble in the cold alcohols. In water and petroleum ether it is insoluble.

A bromine determination by the Pringsheim method[3] slightly modified indicates the compound to be a monobromo guaiacol carbonate. This is apparently a new compound, as it does not seem to be described in the literature.

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[1] Abstracted in *Quart. J. Pharm.*, **1**, 432 (1928); *Apoth. Ztg.*, **43**, 198 (1928).

[2] A. Fernan, *Z. Oesterr. Apoth. Vr.*, **49**, 165 (1911); *C. A.*, **5**, 3324 (1911).

[3] Scott, "Standard Methods of Analysis," D. Van Nostrand Co., Inc., New York, **1917**, 2d ed., revised, p. 122; *Chem. News*, **91**, 215, 2372 (1905). The mixture of substance with sodium peroxide was heated slowly in a nickel crucible until melted. The contents was then allowed to cool and the whole plunged into water.