Summary

1. A method for the preparation of cytosine derivatives alkylated in the (1) position has been described. Methyl iodide interacts with 4-amino-2-methoxypyrimidine to form 4-amino-2-methoxypyrimidine-1-methiodide which can be converted by a number of procedures to 1-methylcytosine.

2. The thermal decomposition of the methiodide proceeds in two directions (1) degradation to 1-methylcytosine with liberation of methyl iodide and (2) the formation of 1-methylcytosine-3-methiodide probably by intramolecular rearrangement.

3. Interaction of 1-methylcytosine and methyl iodide yielded 1 - methylcytosine - 3 - methiodide, from which 1,3-dimethylcytosine was prepared by treatment with alkali.

4. 4 - Amino - 2 - methoxypyrimidine on heating at 180° rearranged to form 1-methylcytosine.

5. Attempts to introduce glucose in the (1) position of cytosine by the interaction of acetobromoglucose and 4 - amino - 2 - methoxypyrimidine were unsuccessful.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Chemistry of the Triethylsilicyl Group

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I. Introduction

The groups of the type R_3A, where R is an organic group or, occasionally, hydrogen, and A an element of the fourth group of the periodic system, exhibit marked amphoteric properties. Thus, on the one hand, they form compounds with the halogens of the type R_3AX, which exhibit electropolar properties[1] to some extent, and compounds with the alkali metals of the type R_3AM, which exhibit marked electropolar properties.[2] With increasing atomic number, the compounds R_3AX become more electropolar although never strongly so. On the other hand, the compounds R_3AM are in all cases strongly electropolar and there is no marked change in properties with increasing atomic number.

Save in exceptional cases, the free groups R_3A do not normally exist in a monomeric condition; they ordinarily combine to form dimers. Certain of the triarylmethyls seem to be markedly dissociated into the free groups in solution, but the corresponding derivatives of silicon, germanium and tin do not seem to be markedly dissociated in solution under ordinary conditions. Evidence, however, exists that goes to show that as the atomic number of the central element increases, the bond joining the groups in the dimer becomes increasingly weak. In boiling benzene, trimethyltin seems to be partially dissociated.[3] In freezing benzene, however, the compound exists as a dimer.[4] The Ge-Ge bond is much more stable than the corresponding Sn-Sn bond. However, even in the case of germanium the bond is readily broken by either strong oxidizing or reducing agents.[5] The Si-Si bond seems to be uncommonly stable and is not broken either by a strong oxidizing agent such as chlorine[6] or reducing agent such as sodium in liquid ammonia or lithium in ethylamine.[7]

With three stable organic groups attached to an element such as silicon, it becomes possible to investigate the properties of the remaining, fourth, valence of that element. While the properties of this residual valence are doubtless more or less influenced by the nature of the substituents R, nevertheless, in the main, they seem to be controlled by the central atom-silicon, germanium or tin. Some work has previously been carried out in this Laboratory on the triphenylsilicyl group[8] and it seemed worth while to extend the study to aliphatic silicon derivatives. One difficulty with the phenylsilicon derivatives is that the compounds seem to break down completely under the action of strong reducing agents.[9]

The corresponding alkyl derivatives, on the other hand, are entirely stable. Accordingly, the

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(1) Kraus and Callis, THIS JOURNAL, **45**, 2624 (1923); Kraus and Greer, *ibid.*, **45**, 2946 (1923).

(2) Kraus and Johnson, *ibid.*, **55**, 2776 (1933); Kraus and Kahler, *ibid.*, **55**, 3537 (1933).

(3) Kraus and Sessions, *ibid.*, **47**, 2361 (1925).

(4) Kraus and Bullard, *ibid.*, **48**, 2131 (1926).

(5) Kraus and Foster, *ibid.*, **49**, 457 (1927).

(6) Meyer and Jacobson, "Lehrbuch der organischen Chemie," Veit and Co., Leipzig, 1907, ed. 2, Vol I, part 1, p. 444.

(7) See Section VIII, below.

(8) Reynolds, Bigelow and Kraus, THIS JOURNAL, **51**, 3067 (1929); Kraus and Eatough, *ibid.*, **55**, 5008 (1933).

(9) Kraus and Rosen, *ibid.*, **47**, 2739 (1925).

present investigation has been directed toward a study of the triethylsilicyl group.

We have studied the behavior of triethylsilane toward potassium amide in liquid ammonia and toward the alkali metals in liquid ammonia and in ethylamine. We have also studied the behavior of triethylsilicon bromide in liquid ammonia and in ethylamine. One of the difficulties experienced in the study of the triethylsilicyl group has been the tendency of its halogen derivatives to ammonolyze in ammonia and ethylamine. We have found it impossible to reduce triethylsilicon bromide either to the free group or to its sodium salt in ammonia or in ethylamine. We have been able to reduce the bromide to the free group or, more properly, to hexaethyldisilane by treating the bromide directly with metallic sodium. To prepare the sodium salt of the triethylsilicyl group, we have had to adopt a roundabout procedure. The triethylsilicyl group was coupled with the triphenylgermanyl group by interaction of triethylsilicon bromide with sodium triphenylgermanide in benzene. On treating triphenylgermanyltriethylsilicon with lithium in ethylamine, a mixture of the lithium salts of the triethylsilicyl and triphenylgermanyl groups was obtained. The existence of lithium triethylsilicide was established by treating the mixture of the two salts with ammonium bromide and ethyl bromide in liquid ammonia, as a result of which triethylsilane and tetraethylsilane were obtained and identified.

II. Materials

In the preparation of the ternary organic derivatives of silicon, silicochloroform is by all means the most convenient starting material. The chloroform may be completely alkylated by means of the Grignard reagent and the hydrogen attached to the silicon atom is then readily substituted by bromine.

Silicochloroform.—Silicochloroform was prepared by the method of Kahler[10] by passing dry hydrogen chloride over ferrosilicon at temperatures between 280 and 300°. The ferrosilicon should be dried carefully prior to carrying out the reaction, as moisture, which is present in considerable quantities, interferes with the reaction.

Dry hydrogen chloride was passed over ferrosilicon in a Pyrex tube and the product of reaction was passed through a trap cooled in liquid ammonia from which the condensate was siphoned into a large distilling flask which was provided with a fractionating column. Several fractionations were carried out in order to get a good separation. With properly controlled conditions, approximately 75% of the initially collected product was recovered as pure silicochloroform; the remaining 25% consisted chiefly of silicon tetrachloride admixed with small quantities of hexachlorodisilane and octochlorotrisilane, as well as traces of some higher derivatives.

Triethylsilane.—Triethylsilane was first prepared by Ladenburg[11] by treating silicon tetraethyl ester with sodium and diethylzinc. Pape[12] prepared tripropylsilane by treating silicochloroform with dipropylzinc. Kahler[10] has shown that triethylsilane may be prepared conveniently by the interaction of the ethyl Grignard reagent with silicochloroform. Since the method is very convenient and we have had occasion to employ it in preparing considerable quantities of triethylsilane, it will be described briefly. The reaction may be carried out either by adding silicochloroform in ether solution directly to the Grignard reagent or by simultaneously mixing the two reagents in nearly equivalent amounts. The latter method gave decidedly the better yields.

After adding the two reagents, the mixture is allowed to stand for fifteen hours and is then boiled with a reflux condenser for twenty hours. Acidulated water is added to decompose the excess ethylmagnesium bromide, the ether layer is separated, dried over calcium chloride and the solvent distilled.

In our preparation the residue was fractionated through a long Eastman column and the product coming over from 100–125° was refractionated, the fraction coming over at 107–110° being retained. The average yield was 56.5%.

Triethylsilane is a colorless liquid with a faint garlic-like odor. It distils without decomposition at 107–110°. It is practically insoluble in liquid ammonia and in water but is very readily soluble in ethylamine.

III. Reaction of Triethylsilane with Potassium Amide in Liquid Ammonia

When triphenylmethane is treated with sodium or potassium amide in liquid ammonia, reaction takes place according to the equation[9]

$$(C_6H_5)_3CH + MNH_2 = (C_6H_5)_3CM + NH_3$$

It might be expected that a similar reaction would take place in the case of triethylsilane. Such, however, is not the case. Triethylsilane reacts with potassium amide in liquid ammonia with evolution of hydrogen. A preliminary study indicated that two moles of the silane react with one mole of potassium amide with the evolution of two moles of hydrogen. A detailed study shows that reaction takes place according to the equation

$$2(C_2H_5)_3SiH + KNH_2 = [(C_2H_5)_3Si]_2NK + 2H_2 \quad (1)$$

Apparatus

The apparatus is outlined in Fig. 1. The reaction was carried out in the tube A, which was cooled in a bath of

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(10) *Unpublished observations by W. H. Kahler, in this Laboratory.*

(11) Ladenburg, *Ann.*, **164**, 300 (1872).

(12) Pape, *ibid.*, **222**, 354 (1883).

liquid ammonia (not shown). The potassium was filled into weighed tubes having an internal diameter of about 1.5 mm. These tubes were cut into suitable lengths and introduced into the addition tube B. Previous to introducing the metal, the reaction tube was exhausted and filled with ammonia and a stream of ammonia was kept issuing from C while the metal was being introduced. The silane was weighed into the tube D which was attached to the apparatus by means of de Khotinsky cement. After condensing the desired amount of liquid ammonia in the reaction tube, the metal was introduced by turning the addition tube through the necessary angle around the axis of the ground joint O. A bit of oxidized iron wire served to facilitate the conversion of the metal to the amide. With stopcock E closed and FF open, ammonia vapor was passed over the silane and thence into the reaction tube through the stirring tube G. Gases evolved in the course of the reaction passed out through the stopcock H and the mercury trap I and were collected over water in J. From J the gases were transferred to the receiver K by means of the Toepler pump L, being dried in the meanwhile by passing through a phosphorus pentoxide tube M. The gases were finally transferred to a density bulb N and the total volume and mean molecular weight determined. The course of the reaction was readily followed by the evolution of gas. In one experiment, after adding one equivalent of triethylsilane to the potassium amide, reaction continued throughout the addition of a second equivalent and it was necessary to add still a little more silane in order to complete the reaction. The reason for the excess of silane was that it is sufficiently volatile at liquid ammonia temperatures so that appreciable amounts are carried over with the escaping gases.

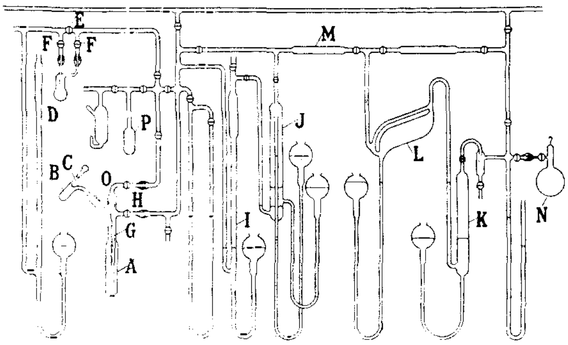

Fig. 1.—Assembly of apparatus.

The data for one such reaction follow: K, 0.3737 (9.56 m. moles); total silane, 2.557 (22.01 m. moles); volume of gas (N. T. P.), 460.6 cc.; mol. wt., 3.32; volume of gas (corr. for air), 438.6 (19.52 m. moles); calcd., equation (1), 428.3 (19.12 m. moles); wt. of residue, 2.6423; calcd. for $[(C_2H_5)_3Si]_2NK$, 2.7092.

The results indicate that reaction proceeded according to equation (1).

If the original potassium di-triethylsilicylamide, or the corresponding amine, is treated with water, it is converted to di-triethylsilicyl oxide. The identity of the oxide was established by its boiling point 231°, and its molecular weight in benzene, which was found to be 241 as against 246.4 required.

IV. Di-triethylsilicylamine

The potassium salt of di-triethylsilicylamine, which is formed in the above reaction, is extremely soluble in liquid ammonia. On adding ammonium bromide to a solution of this salt, the amine is precipitated in the form of a finely divided liquid which gradually coagulates. The amine, as might be expected, is very readily hydrolyzed by moisture and it was therefore necessary to separate it from the reaction mixture by distillation. The reaction tube shown in Fig. 1 was replaced by a second shown in Fig. 2. After preparing the salt and adding ammonium bromide, the ammonia was evaporated. Stopcocks B and F were closed and the apparatus was exhausted through stopcock C. A steam jacket was placed around the reaction tube A and the bulb D was cooled in an ice-bath. The amine distilled out of the reaction tube and collected in the bottom of D. Prior to assembling the apparatus, weighed bulbs E with long capillaries had been introduced into D. When all of the liquid had been collected in D, nitrogen was introduced, which forced the liquid into the bulbs. The tube D was then detached, the bulbs were removed and sealed, the capillaries were cleaned and, together with the bulbs, were weighed. This gave known samples of material in the bulbs, which were sufficiently fragile so that they could be readily broken.

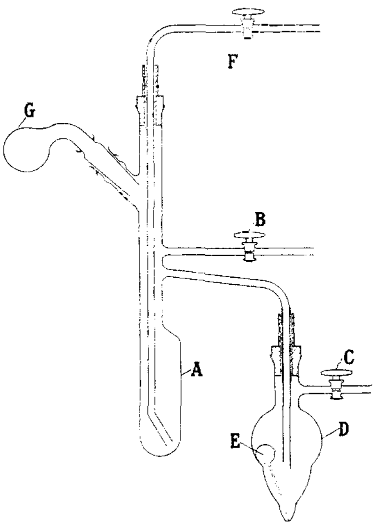

Fig. 2.—Apparatus for preparing known samples.

The amine was analyzed for both silicon and nitrogen. The silicon content was determined by oxidizing a sample in a weighed Pyrex test-tube with fuming nitric and sulfuric acids. After fuming off the acids, the test-tube was reweighed.

Anal. Calcd. for $[(C_2H_5)_3Si]_2NH$: Si, 22.87. Found: Si, 22.59, 22.66.

To determine the nitrogen, a bulb containing the sample was broken under 50 cc. of 6 *N* hydrochloric acid and the mixture was refluxed for thirty minutes. After cooling to room temperature, petroleum ether was added to dissolve the floating oil. The layers were separated, the ether layer was washed with water and the aqueous layer, combined with the washings, was evaporated to dryness in a tared platinum dish. The ammonia was thus determined as ammonium chloride. The residue in the dish was dissolved in water, treated with caustic soda and the ammonia was boiled off and collected in the usual manner in standard hydrochloric acid.

Anal. Calcd. for $[(C_2H_5)_3Si]_2NH$: N, 5.71. Found: (as NH_4Cl)N, 5.38, 5.63; (Kjeldahl) N, 5.06, 5.43.

The molecular weight of the compound was determined cryoscopically in benzene: subs., 0.8856, 0.3570; solvent, 28.87, 27.90; Δt, 0.630, 0.264; mol. wt. found, 243, 242; calcd. for $[(C_2H_5)_3Si]_2NH$, 245.4.

Properties.—Di-triethylsilicylamine is a clear, colorless oil with a faint camphor-like odor. It is insoluble in and heavier than liquid ammonia and distils at 100° under a pressure of 1 mm. Upon hydrolysis, di-triethylsilicyl oxide is formed. The potassium salt of the amine is crystalline, colorless and very soluble in liquid ammonia.

V. Action of Lithium upon Triethylsilane in Ethylamine

It might be expected that in ammonia or ethylamine solution the alkali metals would interact with triethylsilane according to the equation

$$(C_2H_5)_3SiH + Li = (C_2H_5)_3SiLi + {}^1/_2H_2 \tag{2}$$

Such a reaction occurs slowly in the case of triphenylmethane in liquid ammonia solution and more rapidly and quantitatively with monogermane and the alkali metals in ammonia solution.[13]

Since triethylsilane is very slightly soluble in liquid ammonia, ethylamine, in which lithium is fairly soluble, was employed as solvent. It was found, however, that, while reaction occurred readily, the amount of hydrogen evolved was twice that required according to equation (2). Moreover, the lithium itself seemed to take no direct part in the reaction. Upon investigation, it developed that reaction occurs as follows

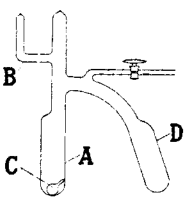

Fig. 3.—Apparatus used in reaction of triethylsilane and ethylamine in the presence of lithium.

$$(C_2H_5)_3SiH + C_2H_5NH_2 + Li = (C_2H_5)_3SiNHC_2H_5 + H_2 + Li \tag{3}$$

The reaction is a homogeneous one and the lithium evidently serves merely as catalyst. The rate of the reaction increases with increasing concentration of lithium.

Several reactions were carried out in an apparatus of the type shown in Fig. 3, which was attached to the system shown in Fig. 1 in place of reaction tube A. A weighed sample of triethylsilane in a fragile bulb C was introduced into arm A of the two-legged reaction tube and lithium, cut under oil into convenient small pieces, was introduced into the side arm B which was then sealed. After exhausting, the tube was detached and the bulb of triethylsilane was broken, whereupon the tube was reattached to the apparatus and ethylamine was condensed on the silane. By gently tapping the tube, lithium was introduced into the ethylamine. Hydrogen was evolved as soon as the blue color due to lithium developed in the solution. When reaction was complete, the hydrogen was removed by means of a Toepler pump, the excess ethylamine was distilled and collected in the ampule P (Fig. 1) and the reaction tube was exhausted. On cooling the arm D of the reaction tube in liquid ammonia, a liquid condensed which was later shown to be triethylsilicylethylamine. Metallic lithium was left behind in the arm A.

The data relating to several reactions were: $(C_2H_5)_3SiH$, 0.8968 (7.77 m. moles), 1.9873 (17.1 m. moles); Li, 0.0549 (7.9 m. at.), 0.0119 (1.71 m. at.); total gas (N. T. P.), 182.6, 384.6 cc.; mol. wt., 2.63, 2.09; volume of gas (corr.) found, 178.3, 383.3 cc.; volume of gas calculated for equation (3), 172.9, 382.5.

It will be noted that, while in the second experiment the total volume of gas is in close agreement with that calculated for equation (3), the amount of metal actually employed was only one-tenth of one atomic equivalent per mole of the silane. The lithium itself obviously takes no direct part in the reaction.

Triethylsilicylethylamine.—This compound was prepared according to reaction (3), using apparatus similar to that outlined in Fig. 2, except that, instead of the addition tube G, the lithium was introduced into a side arm similar to B of Fig. 3. The triethylsilane was introduced in a fragile bulb and, after breaking the bulb, ethylamine was condensed in the reaction tube and the lithium added. When the reaction was complete, the ethylamine was distilled and recovered, the apparatus was exhausted and the triethylsilicylethylamine distilled and filled into fragile bulbs by the procedure described in the preceding section (Fig. 2). To determine the nitrogen content of the compound, a fragile bulb containing a weighed sample was broken under 100 cc. of 2 *N* hydrochloric acid and the mixture was distilled with steam to remove the organic matter. The residual acid solution was filtered and evaporated to dryness in a tared platinum dish and the ethylamine determined as ethylamminohydrochloride. As a check, the residue was redissolved and the chlorine determined as silver chloride.

Anal. Calcd. for $(C_2H_5)_3SiNHC_2H_5$: N, 8.80. Found: (N as ethylamminohydrochloride) N, 9.09, 9.05; (as AgCl) N, 8.78, 9.02.

The oil obtained from the above sample by steam distillation was identified as triethylsilol by its boiling point, 153–155°.

The compound was analyzed for silicon by oxidation to SiO_2 in the usual way.

Anal. Calcd. for $(C_2H_5)_3SiNHC_2H_5$: Si, 17.62. Found: (SiO_2 method), Si, 17.92, 17.73.

The molecular weight of triethylsilicylethylamine was determined cryoscopically in benzene: Solute, 0.4032, 0.4496, 0.4387; solvent, 21.16, 21.91, 21.91; Δt, 0.608,

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[13] Kraus and Kawamura, THIS JOURNAL, **45**, 2756 (1923); E. Seaton Carney, Thesis, Brown University, 1928.

0.630, 0.619; mol. wt. found, 157, 163, 162; calcd. for $(C_2H_5)_3SiNHC_2H_5$, 158.2.

Triethylsilicylethylamine is a clear, colorless liquid with a very penetrating camphor-like odor. It hydrolyzes readily with the formation of triethylsilol. It is soluble in ethylamine and is readily distilled under reduced pressure. It does not react with lithium in ethylamine solution.

VI. Reactions of Triethylsilicon Bromide with Ethylamine and Lithium

Generally, the trialkyl or aryl tin or germanium halides dissolve in ethylamine without ammonolysis and when treated with an alkali metal in this solvent are reduced either to the free groups or, in the presence of excess metal, to the alkali metal salts of these groups. It was hoped that triethylsilicon bromide would not ammonolyze in ethylamine and that, therefore, it might be reduced by means of metallic lithium. It was found, however, that ammonolysis occurs. When a solution of the bromide is treated with metallic lithium, one equivalent of hydrogen is evolved per mole of the original bromide and triethylsilicylethylamine is formed according to the equation

$$(C_2H_5)_3SiBr + C_2H_5NH_2 + Li = (C_2H_5)_3SiNHC_2H_5 + LiBr + {}^1/_2\,H_2 \quad (4)$$

Preparation of Triethylsilicon Bromide.—A solution of 8 cc. of bromine in 90 cc. of ethyl bromide was slowly added to a solution of 16 g. of triethylsilane in 60 cc. of ethyl bromide cooled in an ice-bath. Reaction proceeded rapidly with the evolution of hydrogen bromide. The mixture was refluxed for five hours after which the solvent was distilled. The residue was distilled under reduced pressure yielding 25 g. of triethylsilicon bromide, boiling at 66–67° under 24 mm. pressure, a yield of 93%.

Triethylsilicon bromide is extremely sensitive to moisture and is best handled under exclusion of the atmosphere. The product was filled into weighed fragile bulbs in an apparatus somewhat similar to that outlined in Fig. 2.

Identification of Products.—In a reaction carried out for the identification of hydrogen, using 7.23 m. moles of triethylsilicon bromide and 7.57 m. moles of lithium, 3.54 m. moles of hydrogen was obtained against a calculated yield of 3.62 m. moles required according to equation (4).

Triethylsilicylethylamine was analyzed for nitrogen by hydrolyzing the compound under hydrochloric acid and determining the halogen of the resulting ethylamine hydrochloride. The silicon was determined in the usual way as SiO_2.

Anal. Calcd. for $C_2H_5SiNHC_2H_5$: N, 8.80. Found: (N in ethylamine hydrochloride) N, 8.78, 8.82. Calcd. for $(C_2H_5)_3SiNHC_2H_5$: Si, 17.62. Found: Si, 17.74, 17.69.

The compound resulting from the above reactions was identical with that formed by the interaction of triethylsilane and ethylamine in the presence of metallic lithium.

VII. Lithium Triethylsilicide

Since lithium triethylsilicide could not be prepared by the direct reduction of triethylsilicon bromide with lithium in ethylamine, the preparation of this compound was attempted by more roundabout methods. It was thought that in phenyl- or benzyl-triethylsilane, the phenyl or benzyl groups might be split off by means of metallic lithium in ethylamine solution. The compounds were prepared and their reactions toward lithium in ethylamine were studied. It was found, however, that complex reactions occur, seemingly without the formation of lithium triethylsilicide. Hexaethyldisilane was also prepared, but this compound showed no signs of reaction with lithium in ethylamine.

Finally, the triethylsilicyl group was coupled with the triphenylgermanyl group by treating sodium triphenylgermanide with triethylsilicon bromide in benzene solution. This led to the formation of triphenylgermanyltriethylsilane, which compound was identified. On treating this compound with lithium in ethylamine, the Ge–Si bond was split with the formation of the lithium salts of the triphenylgermanyl and the triethylsilicyl groups. The two salts could not be separated and identified as such, but their existence was demonstrated by reaction of the mixture of salts with suitable reagents and identification of the products. On treating the salt mixture with ammonium bromide, triethylsilane and triphenylgermane were identified, while, on treating with ethyl bromide, tetraethyl-silicon and ethyltriphenylgermanium were identified.

Triphenylgermanyltriethylsilane.—The preparation was carried out in a reaction tube of the type shown in Fig. 3. A weighed sample of triethylsilicon bromide in a fragile bulb was introduced into leg D of the reaction tube and an equivalent amount of triphenylgermanium was introduced into leg A. An equivalent quantity of sodium was introduced into an addition bulb (G, Fig. 2). After condensing ammonia on the triphenylgermanium, the sodium was added. Completion of the reaction was indicated by the disappearance of the difficultly soluble triphenylgermanium and the formation of a yellow solution. The ammonia was evaporated and, after sealing the top of the reaction tube, it was evacuated with a high vacuum pump in order to remove the residual ammonia as completely as possible. Benzene was then condensed in arm A through the stopcock. The bulb containing the triethylsilicon bromide was now broken, benzene was condensed on the bromide and the solution decanted into the solution of sodium triphenylgermanide in arm A. Reaction took place immediately, the coarse lumps of sodium triphenylgermanide gradually disappeared and a white precipitate, presumably of sodium chloride, was formed. The mixture was thoroughly shaken and allowed to stand overnight and the benzene solution was boiled under a pressure of nitrogen for several hours to complete the reaction and to coagulate the precipitate. After distilling the solvent, the last traces were removed by heating under reduced pressure. A moist, yellow solid remained which was dissolved in low boiling petroleum ether and filtered to remove traces of triphenylgermanium, which is insoluble in petroleum ether. The residue, after evaporating the solvent, was placed in an extraction thimble, and washed several times with cold ethyl alcohol, which removed all but a trace of yellow color. It was then extracted with hot alcohol. Upon cooling, triphenylgermanyltriethylsilane crystallized out in clusters which melted sharply at 93.5°. The yield in several experiments varied from 70 to 80% of the theoretical.

The compound was analyzed for germanium and silicon in the following manner. A sample of the compound was oxidized with fuming sulfuric and nitric acids in a weighed test-tube and the weight of the mixed oxides was determined. The amount of germanium oxide in the mixture was determined by a combination of the methods used by Buchanan,[14] Dennis and Papish,[15] Johnson and Dennis,[16] and Foster.[17] The residue in the test-tube was extracted with 6 N sodium hydroxide to dissolve the germanium oxide. The solution was neutralized with concentrated sulfuric acid, transferred to a special distilling apparatus, cooled, made 6 normal with respect to hydrochloric acid and the mixture distilled in a stream of nitrogen. The distillate was caught in a filter flask containing 6 N hydrochloric acid and the germanium was precipitated as sulfide by means of hydrogen sulfide. After filtering and washing the sulfide, it was washed into a small flask and the washings were concentrated. Finally, the sulfide and the few cubic centimeters of solution remaining were washed into a weighed crucible, treated with concentrated nitric acid, evaporated to dryness and ignited to constant weight. The germanium content having been determined, the content of silicon was determined by difference.

Anal. Calcd. for $(C_6H_5)_3Ge\text{-}Si(C_2H_5)_3$: Ge, 17.33; Si, 6.70. Found: Ge, 17.48, 17.38; Si, 6.82, 6.70.

The molecular weight of the compound was determined by the cryoscopic method in benzene: solute, 0.3850, 0.3291, 0.2282, 0.2380; solvent, 14.83, 14.83, 18.28, 18.28; Δt, 0.321, 0.278, 0.160, 0.167; mol. wt. found, 404, 399, 390, 390; calcd. for $(C_6H_5)_3Ge\text{-}Si(C_2H_5)_3$, 419.0.

Properties.—Triphenylgermanyltriethylsilane crystallizes readily from ethyl alcohol in clusters of crystals that melt at 93.5°. The compound is very soluble in benzene and petroleum ether, moderately soluble in hot ethyl and methyl alcohols, but only slightly soluble in cold alcohol. It is practically insoluble in liquid ammonia and slightly soluble in ethylamine at −33°, but is readily soluble in this solvent at higher temperatures.

Reactions of Lithium Triethylsilicide.—A mixture of lithium triethylsilicide and lithium triphenylgermanide was prepared in ethylamine solution as described above. The solution is yellow in color and is stable. However, when the solvent is evaporated and the residue is exhausted for a considerable period of time at room temperatures or above, decomposition seems to occur, since there is a considerable loss in weight.

After distilling most of the ethylamine, liquid ammonia was condensed in the reaction tube. The products of the original reaction dissolved in liquid ammonia to form a yellow solution. On adding ammonium bromide, the yellow color of the solution was rapidly discharged and an oil was precipitated. On completion of the reaction, a clear, colorless solution remained in which were dispersed globules of a colorless oil along with particles of a white solid.

A quantity of alcohol was added to the liquid ammonia solution, the cooling bath was removed and the solution was brought to room temperature by addition of water. This procedure was adopted in order to avoid the loss of triethylsilane through volatilization of the ammonia. The resulting mixture was extracted with ether and the ether evaporated. From the residue was obtained a distillate which was identified as triethylsilane by its boiling point 100–112°. The viscous oil which remained in the distilling flask was volatilized at about 125° under a pressure of 0.01 mm. When the product of this distillation was treated with bromine, vigorous reaction occurred with the evolution of hydrogen bromide. Triphenylgermanium bromide, melting at 137°, was identified as the main product, indicating that the viscous oil consisted chiefly of triphenylgermane. According to Kraus and Foster this substance exists in two solid forms melting at 27° and 47°, respectively, but it is crystallized with considerable difficulty.

A mixture of lithium triethylsilicide and lithium triphenylgermanide, prepared as before, was treated with ethyl bromide. After washing out the salts with water, the residue was extracted with ether. After distilling the ether, an oil was separated from the residue by vacuum distillation and was identified as tetraethylsilicon by its boiling point, 154°. The residue, after distillation, was identified as ethyltriphenylgermanium, m. p. 77.5°.

The reactions of the product of the original reduction with ammonium bromide and ethyl bromide establish the existence of lithium triethylsilicide and lithium triphenylgermanide in solution. These data further establish the nature of the original compound between the triethylsilicyl and triphenylgermanyl groups.

VIII. Some Other Silicon Compounds

As already mentioned, we had occasion to prepare benzyltriethylsilicon. Since this compound is not recorded in the literature, its preparation may be briefly described.

Benzyltriethylsilicon was prepared by two methods: (1) by the action of the ethyl Grignard reagent on benzylsilicon trichloride, the latter compound having been prepared according to the method of Melzner;[18] (2) by treating triethylsilicon bromide with benzylmagnesium chloride. The first method gave a yield of 40% and the

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[14] Buchanan, *J. Ind. Eng. Chem.*, **8**, 585 (1916); *ibid.*, **9**, 661 (1917).

[15] Dennis and Papish, THIS JOURNAL, **43**, 2132 (1921).

[16] Johnson and Dennis, *ibid.*, **47**, 790 (1925).

[17] Unpublished observations by L. S. Foster, in this Laboratory.

[18] Melzner, *Ber.*, **41**, 3390 (1908).

second of 50%. The second preparation, moreover, is much the more convenient, and will be described.

Benzylmagnesium chloride was prepared from 12.6 g. of benzyl chloride and 2.4 g. of magnesium in 100 cc. of anhydrous ether. To this solution, cooled to 0°, was slowly added 10 g. of triethylsilicon bromide in 50 cc. of ether, the mixture being stirred vigorously. The reaction mixture was allowed to stand for fifty hours and was then refluxed for twenty hours, after which the excess Grignard reagent was destroyed with water. The ether layer was evaporated and dried over calcium chloride. After removing the solvent, the residue was fractionally distilled under reduced pressure and the product redistilled at atmospheric pressure. There was obtained 5.5 g. of a colorless oil which boiled without decomposition at 267–269° (corr.), a yield of 50%. The silane was analyzed for silicon by the usual method.

Anal. Calcd. for $(C_2H_5)_3SiC_6H_5CH_2$: Si, 13.61. Found: Si, 13.65, 13.58.

The molecular weight was determined cryoscopically in benzene: solute, 0.3462, 0.3759; solvent, 17.58; Δt, 0.467, 0.504; mol. wt. found, 210, 212; calcd. for $(C_2H_5)_3SiC_6H_5CH_2$, 206.2.

Benzyltriethylsilicon is a clear, colorless oil with an odor resembling that of dibenzyl. It boils without decomposition at 267–269° under atmospheric pressure. It is insoluble in liquid ammonia but very soluble in ethylamine. It does not freeze at −33°.

Benzyltriethylsilicon reacts fairly readily with lithium in ethylamine, without evolution of gas, to yield a clear, deep red solution. No indication of the formation of toluene was observed. The weight of the residue, after evaporating the solvent and treating with liquid ammonia and in turn evaporating the ammonia, was greater than the weight of the original reactants. On adding ammonium bromide to the solution in liquid ammonia, an oil was precipitated. After evaporating the ammonia, the residue was extracted with petroleum ether and the solvent removed. An oil was obtained which boiled at 258°, indicating that it might be a compound in which the benzyl group had been reduced (hydrogenated).

Hexaethyldisilane.—The only preparation of this compound recorded in the literature is that of Friedel and Ladenburg.[19] who obtained it by the action of diethylzinc on silicon tetraiodide. We have found that the compound may be prepared readily by the direct reduction of triethylsilicon bromide by means of sodium. A sample of triethylsilane, 5.4 g., was brominated, the solvent removed and the triethylsilicon bromide transferred to a dry tube containing four equivalents of metallic sodium. The tube was sealed and heated in an oil-bath for ten hours at 140–145°. Reaction proceeded rapidly when the sodium melted. After cooling the tube, the residue was distilled *in vacuo*, yielding two fractions, namely: 0.21 g. of liquid with an odor resembling that of camphor, and 4.15 g. of liquid with an odor similar to that of triethylsilane. The second fraction was fractionated at atmospheric pressure, yielding 2.86 g. of a colorless liquid which boiled, without decomposition, at 255° (corr.), a yield of 54%.

The hexaethyldisilane was analyzed for silicon in the usual manner.

Anal. Calcd. for $[(C_2H_5)_3Si)]_2$: Si, 24.37. Found: Si, 24.20, 24.31.

The molecular weight of the compound was determined by the cryoscopic method in benzene solution: solute, 0.3761, 0.2366; solvent, 20.43; Δt, 0.409, 0.246; mol. wt., 225, 235; calcd. for $[(C_2H_5)_3Si]_2$, 230.4.

Hexaethyldisilane is a colorless liquid, boiling without decomposition at 255° under atmospheric pressure. It is insoluble in liquid ammonia but very soluble in ethylamine. It does not react with sodium in liquid ammonia or with lithium in ethylamine.

Phenyltriethylsilicon.—This compound is readily prepared by the action of ethylmagnesium bromide on phenylsilicontrichloride according to the method of Bygden.[20] It is interesting to note that attempts to prepare this compound by the action of phenylmagnesium bromide or diphenylzinc on triethylsilicon bromide proved unsuccessful.

Metallic sodium does not react with phenyltriethylsilicon in liquid ammonia, probably because of the insolubility of the silicon compound. In ethylamine, lithium reacts readily without the evolution of gas and with the formation of a clear, orange colored solution. No evidence was found indicating the formation of benzene. The weight of the residue, after evaporating the solvent, was found to be greater than that of the original reactants. On adding ammonium bromide to a suspension of the residue in liquid ammonia, an oil was thrown down, which, after extraction with petroleum ether and distillation, boiled at 236–238°. The phenyl group evidently was not split off by the lithium. It is possible that hydrogenation occurred.

Summary

Triethylsilane reacts with potassium amide in liquid ammonia solution according to the equation $2(C_2H_5)_3SiH + KNH_2 = [(C_2H_5)_3Si]_2NK + 2H_2$.

Treated with ammonium bromide in liquid ammonia solution, the potassium salt is converted to di-triethylsilicylamine, which has been characterized.

Triethylsilane in the presence of lithium in ethylamine reacts according to the equation: $(C_2H_5)_3SiH + Li + C_2H_5NH_2 = (C_2H_5)_3SiC_2H_5NH + H_2 + Li$. The lithium merely acts as catalyst and remains at the end of the reaction. The triethylsilicylethylamine has been characterized.

Triethylsilicon bromide ammonolyzes in ethylamine solution. Triethylsilicylethylamine has been identified as the product of ammonolysis.

The triethylsilicyl group has been coupled with the triphenylgermanyl group by the interaction of triethylsilicon bromide with sodium triphenylgermanide in benzene solution. The resulting compound has been characterized and some of its reactions studied.

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(19) Friedel and Ladenburg, *Ann.*, **203**, 241 (1880).

(20) Bygden, *Ber.*, **45**, 709 (1912).

Bromine reacts with triphenylgermanyltriethylsilicon with the formation of triphenylgermanium bromide and triethylsilicon bromide. Lithium reacts with the same compound in ethylamine solution with the formation of an equimolar mixture of lithium triethylsilicide and lithium triphenylgermanide. The mixture of these two salts reacts with ammonium bromide to yield triethylsilane and triphenylgermane and with ethyl bromide to yield tetraethylsilicon and ethyltriphenylgermanium.

Benzyltriethylsilicon has been prepared and characterized. An improved method for the preparation of hexaethyldisilane is described.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF OKLAHOMA]

Chlorine Derivatives of 4-Hydroxydiphenyl

BY J. C. COLBERT, WYMAN MEIGS AND BROWN MACKIN

While the bromination of 4-hydroxydiphenyl[1] has been exhaustively investigated, the action of chlorine upon this phenol appears to have been neglected. Raiford and Colbert[2] found that in carbon disulfide solution bromine entered the two ortho positions of 4-hydroxydiphenyl. In chloroform solution, according to Bell and Robinson, bromination followed the so-called normal course *i. e.*, the first bromine atom entered one ortho position, the second entered the remaining ortho position while the third took the 4′-position.

The present investigation was carried out for the purpose of comparing the action of chlorine upon this phenol with that of bromine and to study the influence, if any, of various solvents upon the entry of chlorine into the molecule.

Influence of Time and Solvent upon the Number of Entering Chlorine Atoms.—When chlorine was bubbled through a suspension of 4-hydroxydiphenyl in a large volume of chloroform, in carbon disulfide and in carbon tetrachloride, respectively, until all starting material had dissolved, the same monochloro derivative was obtained in fairly good yield and in quite pure condition. When chlorination was continued for one to three hours after starting material had dissolved, a dichloro compound was formed in each case, but the yield was diminished after two hours. In no case, thus far, have a mono- and a dichloro compound been isolated from the same reaction mixture.

Chlorination in glacial acetic acid solution resulted in but one recognizable product, a trichlorophenol melting at 137°. While the yield was, in this case, 55% on the basis of entry of three chlorine atoms, recrystallization to obtain a constant melting point reduced the yield to 10%. Clearly a mixture was obtained which we have not yet been able to separate. Analogy with the bromination of 4-hydroxydiphenyl indicates the monochloro derivative to be 3-chloro-4-hydroxydiphenyl, the dichloro to be 3,5-dichloro-4-hydroxydiphenyl and the trichloroderivative to be 3,5,4′-trichloro-4-hydroxydiphenyl. Thus the chlorination of this phenol follows the normal course. An investigation into the chlorination and nitration of *m*-hydroxydiphenyl is now under way in this Laboratory.

Action of Bromine upon 3-Chloro-4-hydroxydiphenyl.—Bromination of this compound in carbon tetrachloride yields a monobromo derivative while substitution of acetic acid or carbon disulfide as the solvent leads to the introduction of two bromine atoms. The dibromo derivative is almost certainly 3-chloro-5,4′-dibromo-4-hydroxydiphenyl while the monobromo derivative is very probably 3-chloro-5-bromo-4-hydroxydiphenyl. The possibility of bromine entering the 4′-position rather than the 5 is not to be lost sight of since Hübner[3] reported the formation of 4′-bromo-4-acetylaminodiphenyl by direct bromination of 4-acetylaminodiphenyl. Investigation of this reaction is being continued.

Experimental Part

3-Chloro-4-hydroxydiphenyl.—Twenty grams of 4-hydroxydiphenyl was suspended in 200 cc. of chloroform contained in a 500-cc. round-bottomed flask and chlorine bubbled through for one hour, *i. e.*, to complete solution. The total volume was reduced, under diminished pressure, to 50 cc., 30 cc. of petroleum ether added, the mixture cooled in an ice-bath, filtered, and the crystals washed with petroleum ether; yield 65% of small white prisms, m. p.

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(1) Bell and Robinson, *J. Chem. Soc.*, **130**, 1128 (1927).

(2) Raiford and Colbert, THIS JOURNAL, **47**, 1127 (1925).

(3) Hübner, *Ann.*, **209**, 339 (1881).