(mixed melting point). The filtrate was boiled for a few minutes, acidified with hydrochloric acid (a precipitate appeared) and extracted with ether. Evaporation of the ether left a brown oil which changed into a viscous semi-solid on standing. This substance was not identified.

Summary

The behavior of a tribromomethyl aryl ketone toward potassium iodide, ethylmagnesium bromide, hydrazine hydrate, phenol, acetone, acetophenone and alkali has been studied. All these reagents except alkali cause partial dehalogenation of the tribromomethyl ketone.

A preliminary study of the action of alkali on dibromomethyl aryl ketones is described which indicates that the conversion of these dibromo ketones into substituted mandelic acids may be retarded by steric hindrance.

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Triphenylsilicyl Ethylammine $(C_6H_5)_3Si{\cdot}C_2H_5NH_2$

BY CHARLES A. KRAUS AND HARRY EATOUGH[1]

I. Introduction

The elements of the fourth group form compounds of the type $(R_3A)_2$ where R is commonly an organic radical or, less frequently, hydrogen. The bond A–A has a varying stability depending on the nature of the central element and of the substituents R. In some instances, the compounds dissociate into the free groups R_3A in solution, while in others the dimers are relatively stable. Stability usually increases with decreasing atomic number. These groups are amphoteric, forming compounds R_3AX with negative elements or groups and salts R_3AM with electropositive elements such as the alkali metals. Various of the free groups and their reduction products have been investigated in this Laboratory, particularly those of tin, germanium, and carbon.[2] The free groups are ordinarily formed by reducing the halogen derivatives with the alkali metals in liquid ammonia and the salts are formed by further reduction of the resulting free groups. In the case of silicon, it has not been possible, heretofore, to obtain either the free groups (or their dimers $(R_3Si)_2$) or the alkali metal salts $MSiR_3$ by reduction of the halogen derivatives R_3SiX in liquid ammonia. The reason for this is that the tertiary organic halogen derivatives are ammonolyzed in liquid ammonia.

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(1) Rice Fellow in Chemistry at Brown University.

(2) Kraus and Kawamura, THIS JOURNAL, **45**, 2756 (1923); Kraus and Sessions, *ibid.*, **47**, 2361 (1925); Kraus and Foster, *ibid.*, **49**, 457 (1927). For the conductivity of these compounds see Kraus and Callis, *ibid.*, **45**, 2624 (1923); Kraus and Johnson, *ibid.*, **55**, 3542 (1933); Kraus and Kahler, *ibid.*, **55**, 3537 (1933).

It was thought that triphenylsilicon bromide might be reduced to the free group or to its lithium salt by means of lithium in ethylamine, since ethylamine is a much weaker ammonolyzing agent than is liquid ammonia. It was to be expected that triphenylsilicon bromide would be reduced to hexaphenyldisilane in the first instance. The Si–Si bond, however, is very stable and it was not to be expected that this bond would be broken by metallic lithium.

On carrying out the reduction of triphenylsilicon bromide with lithium in ethylamine, reaction occurred without evolution of gas and a soluble product was formed which indicated that reduction, rather than ammonolysis, had taken place. When a second equivalent of lithium was added, a reddish colored solution was formed, indicating the presence of a lithium salt. On evaporating the solvent, after reducing the bromide with one equivalent of lithium, a solid product remained behind which was separated from the inorganic material by distillation at a temperature of 150° in a high vacuum. A well-crystallized solid was obtained which melted at 45°. Analysis indicated that the compound had the formula $(C_6H_5)_3Si\cdot C_2H_5NH_2$, that is, that the product was a molecular compound of the triphenylsilicyl group with one molecule of ethylamine. The molecular weight of the compound in benzene confirmed the results of analysis. The compound appears to be altogether exceptional since it contains an odd number of electrons. Moreover, the compound does not dissociate at 150° in a high vacuum. Because of the unusual nature of the compound, its reactions were carefully studied. Dissolved in boiling ether, the compound dissociates with the formation of hexaphenyldisilane. Treated with water, ethylamine is formed and the silicon compound is left behind. Treated with lithium in ethylamine, lithium triphenylsilicide is formed, which reacts with various reagents as might be expected.

When lithium triphenylsilicide is treated with trimethyltin chloride in liquid ammonia, a reaction occurs in which the tin and silicon atoms are coupled to yield trimethylstannyltriphenylsilicon. The Sn–Si linkage is broken by means of the alkali metals in liquid ammonia or by means of bromine in ordinary solvents.

II. Triphenylsilicyl Ethylammine

Preparation.—A weighed quantity of triphenylsilicon bromide was introduced into the reaction tube A (Fig. 1) and an equivalent quantity of lithium was introduced into the arm B of the reaction tube, whereupon the tube was sealed at G and H. It was then attached to a system similar to that commonly employed in this Laboratory,[3] and exhausted. Fifty cc. of ethylamine, dried with lithium, was condensed in the reaction tube and lithium was added slowly to the ethylamine solution of triphenylsilicon bromide by tapping the side arm B. The lithium went into solution without the appearance of color and without the formation of a precipitate or the evolution of gas. Toward the end, when the reaction slowed down, the contents of the tube were stirred from time to time by boiling the solution.

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[3] Kraus and Nutting, THIS JOURNAL, 54, 1622 (1932).

On completion of the reaction, the ethylamine was distilled into a collecting ampoule and the reaction tube was evacuated. It was then detached from the system, placed in a horizontal position, with the tube C projecting downward, and exhausted by means of a high vacuum pump. A jacket was placed around the tube A and the temperature was raised to approximately 150°. Under these conditions triphenylsilicyl ethylammine condensed in the neck of the reaction tube just beyond the heated portion and, on gently warming the tube, it melted and ran into the receiving tube C.

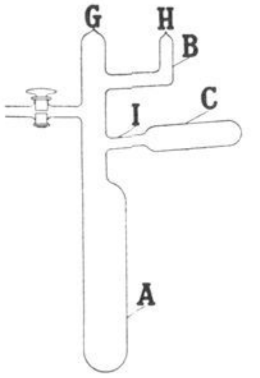

Fig. 1.—Reaction tube used in preparation of triphenylsilicyl ethylammine.

When distillation was completed, the tube was filled with dry nitrogen and the tube C, containing the compound, was sealed off at I. This tube was then introduced into the filling apparatus illustrated in Fig. 2.

A number of weighed, fragile bulbs D with long capillaries were introduced into the expanded tube E (Fig. 2) and the tube C, containing the triphenylsilicyl ethylammine, was introduced into the tube F, the neck of the tube C (previously cut open) projecting downward. The apparatus was exhausted and a bath of hot water was placed around the apparatus to melt the compound, which ran out of its container into the bottom of the expanded tube E. After thoroughly exhausting the apparatus, nitrogen was introduced, which forced the liquid compound through the capillaries into the bulbs. The tube was now allowed to cool and the bulbs were removed, sealed and weighed, along with the capillaries. This gave known samples of the compound for analysis and other purposes.

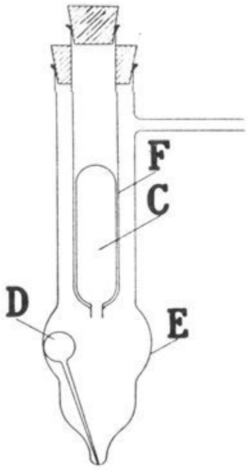

Fig. 2.—Apparatus for preparing weighed samples

Analysis.—It was desirable to analyze for both silicon and nitrogen on the same sample. For this purpose, the sample (in a fragile bulb F) was introduced into a weighed Pyrex tube A (Fig. 3) which, in turn, was introduced into a larger tube B, which was later sealed. The tubes were so fitted that A was held firmly in position. Air-free water was introduced into tube C and the whole apparatus was exhausted. The sample bulb was now broken and the desired quantity of water from C was condensed in A, when the stopcock D was closed. Tubes B and E were then placed in boiling water and heated for four hours in order to complete the dissociation of the compound into ethylamine and hexaphenyldisilane. The aqueous solution of ethylamine was then distilled into the tube E, while the hexaphenyldisilane remained behind in the analysis tube A.

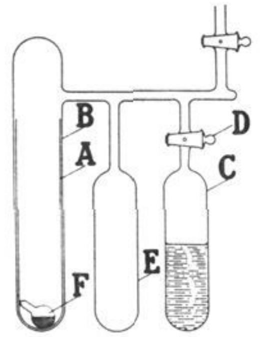

Fig. 3.—Apparatus used in determining ethylamine in triphenylsilicyl ethylammine.

The ethylamine solution was transferred to a beaker and titrated with standard 0.1 *N* hydrochloric acid. After adding a slight excess of acid, the solution was evaporated to dryness and the residue was weighed. This gave the weight of ethylamine hydrochloride. Finally, the hydrochloric acid was redissolved and the chlorine content determined as silver chloride. Tube B was cut open, the analysis tube A was removed and the silicon content of the product was determined by the usual method of oxidation with nitric and sulfuric acids.

Anal. Calcd. for $(C_6H_5)_3Si \cdot C_2H_5NH_2$: N, 4.60; Si, 9.22; mol. wt., 304.2. Found: N (by HCl titration), 4.59, 4.57 (by wt. of $C_2H_5NH_3Cl$), 4.58, 4.57 (by wt. of AgCl), 4.67, 4.66; Si, 9.19, 9.17; mol. wt. (cryoscopic in benzene), 292, 287, 290.

Properties.—Triphenylsilicyl ethylammine is a white, crystalline solid which melts at 45°. It is soluble in all of the ordinary organic solvents with the exception of low boiling petroleum ether and alcohol.

Dissociation of Triphenylsilicyl Ethylammine in Ether.—A solution containing 1.23 g. of triphenylsilicyl ethylammine in 25 cc. of dry ether was distilled to remove the solvent and the residue was evaporated to dryness. The residue was taken up in 25 cc. of dry ether and the solution was filtered. There was obtained 0.29 g. of insoluble material which melted at 351–353° and was thus identified as hexaphenyldisilane. The ether solution was boiled under a reflux condenser for half an hour, after which the solvent was again separated by filtration. In this case, there was obtained 0.71 g. of hexaphenyldisilane, thus, making a total of 1.00 g. as against 1.04 g. calculated. This shows that in solvents at higher temperatures the compound is dissociated with the formation of hexaphenyldisilane.

The ethylamine is not replaced by ammonia at liquid ammonia temperatures. Triphenylsilicyl ethylammine does not react with sodium in liquid ammonia to an appreciable extent. It reacts readily with lithium in ethylamine to form lithium triphenylsilicide.

III. Lithium Triphenylsilicide

Preparation.—Lithium triphenylsilicide is readily formed by the direct action of metallic lithium upon triphenylsilicyl ethylammine in ethylamine solution, reaction taking place as follows

$$(C_6H_5)_3Si{\cdot}C_2H_5NH_2 + Li = (C_6H_5)_3SiLi + C_2H_5NH_2$$

It is readily soluble in ethylamine but only slightly soluble in liquid ammonia. Its solubility in liquid ammonia is greatly increased by the presence of small quantities of ethylamine.

The preparation of lithium triphenylsilicide was carried out in a reaction tube of the type usually employed for such purposes in this Laboratory, except that the reaction tube was not provided with the usual central stirring tube. Triphenylsilicyl ethylammine was introduced in a fragile bulb and lithium, cut in small pieces, was introduced into an addition tube from which it could be added to the solution as desired. After evacuating the reaction tube, the fragile bulb was broken and 30 cc. of ethylamine was condensed. The lithium reacted readily with the formation of a reddish colored solution. When all the lithium had been added, the color was so dense that the solution was opaque. On distilling the ethylamine, a white, crystalline solid remained behind.

Reactions of Lithium Triphenylsilicide.—Since the salt cannot be analyzed directly, its constitution was established indirectly by means of certain typical reactions.

(1) Reaction with Ammonium Bromide.—If lithium triphenylsilicide is present, it should react with ammonium bromide to form triphenylsilicane according to the equation: $(C_6H_5)_3SiLi + NH_4Br = (C_6H_5)_3SiH + LiBr + NH_3$.

Lithium triphenylsilicide was prepared in ethylamine solution as described above and, after evaporating the ethylamine, 25 cc. of ammonia was condensed in the tube. The salt was only slightly soluble, yielding an orange colored solution. On adding ammonium bromide, the color of the solution diminished in intensity while the excess salt went into solution. After evaporating the ammonia, the inorganic material was extracted with water. The organic residue was dried and dissolved in 95% alcohol, from which triphenylsilane crystallized on evaporation of the solvent under reduced pressure. With the small amount of material available, it was difficult to obtain a high degree of purity. Nevertheless, the product melted at 30–33° as against 36–37° for pure triphenylsilane.

(2) Reaction with Phenyl Bromide.—We should expect that lithium triphenylsilicide would react with phenyl bromide to form tetraphenylsilicon according to the equation $(C_6H_5)_3SiLi + C_6H_5Br = (C_6H_5)_4Si + LiBr$.

Lithium triphenylsilicide was prepared as described above; the bulk of the ethylamine was evaporated and ammonia was condensed on the residue. Phenyl bromide was added to the ammonia solution. Reaction took place at once, with disappearance of the orange color due to the lithium salt, and a white precipitate was formed. After evaporating the ammonia, any excess phenyl bromide was extracted with dry ether in which tetraphenylsilicon is insoluble. The tetraphenylsilicon was then extracted with hot benzene. A practically quantitative yield of this compound was obtained which, after crystallization, melted at 230–231°. Polis gives the melting point as 233°.[4]

The above reactions clearly demonstrate the existence of lithium triphenylsilicide. The reactions of this salt are similar to those of corresponding salts of tin, germanium and carbon.

IV. Trimethylstannyltriphenylsilicon

It was to be expected that lithium triphenylsilicide would react with amminotrimethyltin chloride according to the equation

$$(C_6H_5)_3SiLi + (CH_3)_3SnCl{\cdot}NH_3 = (C_6H_5)_3SiSn(CH_3)_3 + LiCl + NH_3$$

Kraus and Foster[5] have prepared a similar compound of germanium and tin which is a white, crystalline solid melting at 88°. The expected silicon compound was obtained as a viscous liquid which could not be crystallized.

Preparation.—Lithium triphenylsilicide was treated with amminotrimethyltin chloride in liquid ammonia. As the chloride was added, the color of the lithium salt disappeared and an oily appearing substance was precipitated. The material in the reaction tube was extracted with petroleum ether (35–55°), the solvent was evaporated on a water-bath and the last traces were removed by means of a vacuum pump. The product was an oily liquid which could not be crystallized even at liquid ammonia temperatures.

The compound was analyzed for combined tin and silicon by oxidation in the usual way. After weighing the combined oxides, the tin oxide was dissolved in concentrated hydrochloric acid and the tin was precipitated as metastannic acid, which was then ignited and weighed as stannic oxide. The weight of the silicon dioxide was determined by difference.

Anal. Calcd. for $(C_6H_5)_3SiSn(CH_3)_3$: Sn, 28.06; Si, 6.63. Found: Sn, 27.65, 27.77; Si, 6.84, 6.69.

Molecular Weight.—The molecular weight of the compound was determined in benzene solution. In all cases the molecular weight was about 50% too high. A series of values was obtained ranging from 599 to 616, while the calculated molecular weight is 423.1. There is no obvious explanation for the discrepancy.

Reactions.—In view of the somewhat unsatisfactory value obtained for the molecular weight, it seemed worth while to characterize the compound somewhat further by its reactions. Accordingly, the following reactions were carried out: (1) reduction by means of sodium in liquid ammonia and subsequent treatment of the products of reduction with methyl iodide; (2) bromination of the compound in ether, separation of the products, and subsequent characterization of the same.

(1).—On treating the compound with sodium in liquid ammonia, one should expect the reaction

$$(C_6H_5)_3SiSn(CH_3)_3 + 2Na = (C_6H_5)_3SiNa + (CH_3)_3SnNa \qquad (1)$$

Reaction proceeded somewhat slowly with the formation of a solution having a yellow color, which is characteristic of the sodium salts of the tertiary alkyl- and aryltin or germanium groups. On adding methyl iodide, the color was discharged and a

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(4) Polis, *Ber.*, **18**, 1541 (1885).

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

precipitate was formed. If reaction proceeds according to equation (1), it would be expected that the following reactions would take place on adding methyl iodide.

$$(C_6H_5)_3SiNa + CH_3I = (C_6H_5)_3SiCH_3 + NaI \qquad (2a)$$

$$(CH_3)_3SnNa + CH_3I = (CH_3)_4Sn + NaI \qquad (2b)$$

On completion of the reaction, about 15 cc. of 95% ethyl alcohol was added to the solution and then water in sufficient quantity so that, when the solution finally warmed to room temperature, its vapor pressure was less than one atmosphere. This procedure was necessary since, if the ammonia had been evaporated directly from the solution, the tetramethyltin formed in reaction (2b) would have been carried away with the vapor. The solution was transferred to a separatory funnel and extracted with ether. After separation, the ether was dried with anhydrous sodium sulfate and distilled. The residue was taken up in fresh ether and precipitated with alcohol. The precipitate was identified as methyltriphenylsilicon by its melting point 67°. The ether distillate, containing tetramethyltin, was treated with a small quantity of bromine, the ether was distilled and the residue dissolved in petroleum ether. On passing ammonia into the petroleum ether solution, a precipitate was formed. This procedure served to characterize the tetramethyltin since it is known that trimethyltin bromide forms an insoluble precipitate with ammonia.[6]

(2).—On treating the compound with bromine, one should expect the Si–Sn bond to be broken with the formation of an equimolar mixture of triphenylsilicon bromide and trimethyltin bromide. The compound was treated with an equivalent quantity of bromine in ether solution in an apparatus so arranged that, after taking off the ether, the trimethyltin bromide could be separated from the triphenylsilicon bromide by distillation *in vacuo*. After separating the two materials, the apparatus was opened and the two products were extracted with ether and weighed. The results were: wt. sample, 0.4036 g.; $(C_6H_5)_3SiBr$ found, 0.3347 g.; calcd., 0.3236; $(CH_3)_3SnBr$ found, 0.2281; calcd., 0.2326.

The trimethyltin bromide was analyzed for bromine by the usual silver bromide method.

Anal. Calcd. for $(CH_3)_3SnBr$: Br, 30.65. Found: Br, 30.55, 30.54.

The triphenylsilicon bromide was hydrolyzed by means of water and the insoluble silicol was weighed. There were obtained 0.2625 g. as against 0.2636 g. required on the basis of the original weight of material. The bromine was determined as silver bromide as follows: $(C_6H_5)_3SiBr$ (calcd.), 0.3236, AgBr, 0.1784; Br found, 23.46. Calcd. for $(C_6H_5)_3SnBr$: Br, 23.57.

The various reactions supply conclusive evidence that the product obtained by the interaction of trimethyltin bromide with sodium triphenylsilicide in liquid ammonia is simply a combination of the triphenylsilicyl and the trimethylstannyl groups.

In conclusion, all the evidence supports the view that the compound obtained upon treating triphenylsilicon bromide with lithium in ethylamine is a combination of the triphenylsilicyl group with one molecule of ethylamine. We have found no evidence of the formation of a similar compound in the case of tin. Some preliminary investigations on the reduction of triphenylsilicon bromide in methylamine indicate the formation of triphenylsilicyl methylammine,[7] which is distinctly more volatile than the corresponding ethylamine derivative.

V. Summary

Triphenylsilicon bromide and metallic lithium react in ethylamine solution according to the equation: $(C_6H_5)_3SiBr + Li + C_2H_5NH_2 =$

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[6] Kraus and Greer, THIS JOURNAL, **45**, 3078 (1923).

[7] F. C. Schmidt, unpublished observations in this Laboratory.

$(C_6H_5)_3Si{\cdot}C_2H_5NH_2$ + LiBr. Triphenylsilicyl ethylammine is a stable compound, melting at 45°, which may be distilled in a high vacuum at 150° without decomposition. In solution in ether and other solvents it decomposes at higher temperatures with the formation of hexaethyldisilane and ethylamine.

It reacts with lithium in ethylamine to form lithium triphenylsilicide. The latter compound reacts with ammonium bromide to form triphenylsilane and with phenyl bromide to form tetraphenylsilicon.

On treating lithium triphenylsilicide with trimethyltin chloride in liquid ammonia solution, the triphenylsilicyl and the trimethylstannyl groups are coupled. This compound is a heavy oil which is stable under ordinary conditions. It reacts with sodium in liquid ammonia to give the sodium salts of the two groups. It reacts with bromine, yielding triphenylsilicon bromide and trimethyltin bromide.

Triphenylsilicyl ethylammine is an exceptional compound in that it has an odd number of electrons and yet is remarkably stable. All the reactions of this compound, however, tend to confirm its constitution as a simple combination of the triphenylsilicyl group with a molecule of ethylamine.

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The Reactions of Sodium Triphenylstannide with Polyhalogenated Methanes

BY CHARLES A. KRAUS AND HARRY EATOUGH[1]

Compounds such as sodium triphenylstannide react quite generally with the alkyl and aryl halides with the formation of the corresponding sodium halide and the coupling of the alkyl or aryl group with the tin of the triphenylstannyl group. However, in the case of halogen derivatives containing more than one halogen, the reactions usually become more complex and a simple substitution of triphenylstannyl or a similar group for the halogen does not ordinarily occur.

Kraus and Nutting[2] have shown that sodium triphenylgermanide reacts with methylene chloride in part with the formation of di-triphenylgermanylmethane and in part with the formation of monotriphenylgermanylmethane. They account for the formation of the latter compound by a reaction in which a valence of the carbon atom is hydrogenated and triphenylgermanylamine is formed. In the case of chloroform, Kraus and Nutting could find no indication of the formation of the tertiary germanyl derivative, although considerable quantities of the di- and mono-germanyl

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[1] Rice Fellow in Chemistry at Brown University.

[2] Kraus and Nutting, THIS JOURNAL, 54, 1622 (1932).