[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

The True Identity of the Solvated Free Radical "Triphenylsilicyl Ethylammine." The Multiple Addition of Lithium to an Aromatic System in Ethylamine

BY ROBERT A. BENKESER, ROBERT E. ROBINSON AND HERBERT LANDESMAN

RECEIVED JUNE 2, 1952

The compound previously reported as the solvated free radical "triphenylsilicyl ethylammine" $[(C_6H_5)_3Si\cdot EtNH_2]$ has been found to be in reality triphenyl-N-ethylaminosilane $(C_6H_5)_3SiNHEt$. When triphenyl-N-ethylaminosilane reacts with lithium in ethylamine, a red solution is formed which contains not the reported triphenylsilyllithium, but rather a multiple addition product with lithium, of the general formula $[(C_6H_5)_3SiNHEt]_nLi$. This addition by lithium is a function of the aromatic ring system since benzene alone in ethylamine absorbs six equivalents of the metal. A mechanism for the formation of triphenyl-N-ethylaminosilane from triphenylbromosilane or triphenylchlorosilane and lithium in ethylamine is given.

Kraus and Eatough[1] report the formation of "triphenylsilicyl ethylammine" through the reaction of triphenylbromosilane with lithium in ethylamine.

$$(C_6H_5)_3SiBr + Li \xrightarrow{EtNH_2} LiBr + (C_6H_5)_3Si\cdot EtNH_2 \left(\begin{array}{c}\text{"triphenylsilicyl}\\ \text{ethylammine"}\end{array}\right) \quad (1)$$

This substance is described as a white, crystalline solid which distils without decomposition and melts at 45°. The chemistry of this material as reported corresponds to that expected for the solvated free radical shown in 1. Thus the compound allegedly dimerizes to hexaphenyldisilane in boiling ether or boiling water, and adds an equivalent of lithium in ethylamine to produce a red solution which supposedly contains triphenylsilyllithium.

In this Laboratory, it was found that both triphenylbromosilane and triphenylchlorosilane react with lithium in ethylamine to give the compound described by Kraus and Eatough. However, most of the reactions of the so-called "free radical" could not be duplicated by us. Further investigation indicated that the "free radical" was neither chemically or physically distinguishable from a compound possessing just one less hydrogen atom, namely, triphenyl-N-ethylaminosilane, $(C_6H_5)_3SiNHEt$. The latter substance can be conveniently prepared through the action of ethylamine on triphenylbromosilane or triphenylchlorosilane in ether.

$$(C_6H_5)_3SiBr + EtNH_2 \xrightarrow{\text{ether}} (C_6H_5)_3SiNHEt + EtNH_3Br \quad (2)$$

Both compounds melt at 47–48° and neither depresses the melting point of the other. Both materials react with water to give triphenylsilanol and hexaphenyldisiloxane. In neither case can any hexaphenyldisilane be detected. Neither compound undergoes any reaction when boiled in ether. Both react with ethylamine hydrochloride in ethylamine to form triphenylchlorosilane. Both react with lithium in ethylamine to give the red solution reported by Kraus and Eatough. This solution, however, gives no reactions characteristic of triphenylsilyllithium. Thus, with bromobenzene no tetraphenylsilane is formed, whereas with ethylamine hydrochloride the product is diphenylbis-(ethylamino)-silane, $(C_6H_5)_2Si(NHEt)_2$, rather than the expected triphenylsilane. On the basis of all this evidence, it must be concluded that the compound reported by Kraus and Eatough has the silicon amine structure $(C_6H_5)_3SiNHEt$ rather than the free radical structure.

The reaction of triphenyl-N-ethylaminosilane with lithium is an unusual one and was investigated at some length. It was found that tetraphenylsilane and triphenylmethylsilane also give the characteristic red solution with lithium in ethylamine; hence the reaction cannot depend on the presence of silicon–nitrogen bonds in the molecule. Indeed, the silicon atom itself cannot be essential, since the red solution is given by benzene but not by tetramethylsilane. The stoichiometry of the reaction was studied by treating a variety of compounds with excess lithium in ethylamine, acidifying the mixture with ethylamine hydrochloride, and measuring the pressure of hydrogen liberated by the excess metal. The results obtained (Table I) indicate that six equivalents of lithium are absorbed for each phenyl group in the molecule. It would appear that complete saturation of the benzene rings by lithium is taking place. A more complete treatment of this subject will appear in future papers.

From the above it is apparent that the red solution described by Kraus and Eatough does not contain triphenylsilyllithium as they report. Obviously the reaction producing this red solution is not restricted to organosilicon chemistry, but is in reality an isolated example of a much more far reaching addition reaction.

It is difficult at first sight to find an adequate explanation for the formation of triphenyl-N-ethylaminosilane in the Kraus–Eatough reaction. Anderson[2] demonstrated that the conversion of a chlorosilane to an aminosilane is a reversible reaction. Thus the interaction of triphenylchloro- or bromosilane and ethylamine should initiate the equilibrium

$$(C_6H_5)_3SiCl + 2C_2H_5NH_2 \rightleftarrows (C_6H_5)_3SiNHC_2H_5 + C_2H_5NH_3Cl \quad (3)$$

Such has been found to be the case. In ether, triphenylchlorosilane is converted to triphenyl-N-ethylaminosilane, the precipitation of the hydrochloride pulling the reaction to the right. In ethylamine, however, all the materials are soluble. The equilibrium is shifted to the left by the distillation of the volatile ethylamine solvent, and triphenylchlorosilane is isolated.

---

[1] C. A. Kraus and H. Eatough, THIS JOURNAL, **55**, 5008 (1933).

[2] H. H. Anderson, *ibid.*, **73**, 5802 (1951).

TABLE I

EQUIVALENTS OF LITHIUM ABSORBED BY VARIOUS COMPOUNDS IN ETHYLAMINE

Compound	Mole	Equiv. Li	Mm. H_2	Volume, liters	Temp., (°K.)	Equiv. Li per mole
$(C_6H_5)_4Si$	0.0020	0.050	65	1.12	298	21.1
$(C_6H_5)_4Si$	.0020	.050	68	1.19	300	20.7
$(C_6H_5)_3SiNHEt$	.00282	.0564	65	0.925	299	17.7
$(C_6H_5)_3SiNHEt$	.00213	.0426	47	0.925	298	17.8
$(C_6H_5)_3SiMe$	.00278	.050	30	1.12	300	16.7
$(C_6H_5)_3SiMe$	.00278	.050	33	1.12	300	16.6
$(C_6H_5)_2SiMe_2$	.00333	.050	73	1.12	300	12.4
$(C_6H_5)_2SiMe_2$	.00333	.050	74	1.12	300	12.3
$(C_6H_5)SiMe_3$	.0050	.050	200	0.950	300	5.9
$(C_6H_5)SiMe_3$	.00625	.050	164	0.925	300	5.4
$SiMe_4$	.020	.020	165	1.12	301	0.0
$(C_6H_5)H$	.00625	.050	109	1.12	299	5.9
$(C_6H_5)H$	.00714	.050	57	1.12	300	6.0

Metallic lithium apparently shifts the equilibrium to the right, but not through direct action with ethylamine hydrochloride since no hydrogen is liberated during the reaction. It is notable that a transient red color generally accompanies the reaction with lithium, although the solution is colorless when all the metal has reacted. This suggests the intermediate formation of a polylithium addition compound.

$$(C_6H_5)_3SiY + nLi \longrightarrow (C_6H_5)_3SiY \cdot nLi \text{ (red)} \quad (4)$$
$$(Y = -Cl \text{ or } -NHEt) \; (n = 1\text{–}18)$$

Such would be expected to react with the ethylamine hydrochloride from the halide–amine equilibrium mixture.

$$(C_6H_5)_3SiY \cdot nLi\text{(red)} + nEtNH_3Cl \longrightarrow (C_6H_5)_3SiY \cdot nH \text{ (colorless)} + nEtNH_2 \quad (5)$$

Thus a species on the right side of equation 3 would be removed, causing the equilibrium to be shifted in that direction. Since a rather large number of lithium atoms may be absorbed by a single organic molecule (Table I), the bulk of the organic material need undergo no reaction with lithium. Hence it would be isolated as triphenyl-N-ethylaminosilane.

The acceptance of this sequence of reactions requires the verification of three important assumptions: (1) that the addition of lithium to an aromatic system (reaction 4), proceeds more rapidly than the reaction of the metal with ethylamine hydrochloride, (2) that with equimolar amounts of aromatic silane and metal, reaction 4 occurs in such a manner that a relatively small fraction of the organic material absorbs most of the metal, the remaining organosilane being unaffected, and (3) that a triphenylhalosilane is converted to triphenyl-N-ethylaminosilane on treatment with an aromatic polylithium compound in ethylamine.

The validity of the first two assumptions was tested by allowing equimolar amounts of organosilane, ethylamine hydrochloride and lithium to react in ethylamine. For the first assumption to hold, little or no hydrogen should be liberated. For the second assumption to be verified, the bulk of the organic material must be recovered unchanged. The reaction was run with both triphenylmethylsilane and triphenyl-N-ethylaminosilane. In the former case, only a small quantity of hydrogen was produced, and in the latter case none at all could be detected. In both cases, well over 50% of the starting material was recovered. To test the third assumption, triphenylbromosilane was added to the solution resulting from the addition of six equivalents of lithium to triphenyl-N-ethylaminosilane. The amount of aminosilane isolated from the reaction mixture was greater than that originally introduced.

As mentioned previously, when triphenyl-N-ethylaminosilane is treated with lithium in ethylamine in the *absence* of ethylamine hydrochloride, a permanent red solution results which yields diphenylbis-(ethylamino)-silane upon treatment with acid.

$$(C_6H_5)_3SiNHEt + Li \xrightarrow{EtNH_2} (C_6H_5)_2Si(NHEt)_2$$

Apparently it is necessary for ethylamine hydrochloride to be present in the reaction mixture *during* the lithium addition for cleavage of phenyl groups to be prevented. This suggests that the highly basic medium in which the addition occurs is responsible for the cleavage. The work of Hance and Hauser[3] on the cleavage of phenylated silanes by potassium amide in liquid ammonia supports this opinion.

Experimental

Apparatus.—Except where otherwise indicated, all reactions were carried out in a small round-bottomed flask, to which was attached a Claisen head, a vacuum adapter, and a receiving flask. All joints were of ground glass. The apparatus was connected through the adapter to the manifold of a high vacuum system. Agitation was obtained through the use of a magnetically operated stirrer. In cases where solids were introduced into reaction mixtures under vacuum, the transfer was effected by condensing the solvent upon the solid in an extraction thimble and allowing the solution to flow into the reaction vessel. Pressures down to 10^{-6} mm. were employed.

Triphenyl-N-ethylaminosilane.—To 6.0 g. (0.177 mole) of triphenylbromosilane[1] dissolved in 200 ml. of anhydrous ether was added a solution of excess ethylamine in anhydrous ether. The mixture was placed in a round-bottomed flask with an attached Friedrich condenser equipped with a P_2O_5 drying tube. The mixture was shaken for 10 minutes and the precipitate which formed was allowed to settle. The solution was then filtered[4] rapidly by suction. The filter cake was washed several times with anhydrous ether and the combined filtrates evaporated under P_2O_5 drying tubes. The solid residue remaining after removal of the ether was distilled through a Claisen head at 163–165° at 0.5 mm. The product solidified in the receiver and was found to melt at 47–48°. The material was stored in a vacuum desiccator over P_2O_5.

Anal. Calcd. for $C_{20}H_{21}NSi$: Si, 9.24; N, 4.62. Found: Si, 9.46; N, 4.38.

Repetition of the Kraus–Eatough Reaction.—The reaction was carried out in the vacuum reactor described by Kraus and Eatough[1] as well as in the apparatus described above. Both triphenylchlorosilane and triphenylbromosilane were used as starting materials. In all cases the same results were obtained. In a typical run, 35 ml. of anhydrous ethylamine was condensed on 10.0 g. (0.029 mole) of triphenylbromosilane and 0.2 g. (0.029 atom) of lithium.[5]

---

[3] C. R. Hance and C. R. Hauser, THIS JOURNAL, **74**, 1856 (1952).

[4] The precipitate obtained at this point was washed carefully with ether and then crystallized from alcohol–ether. It was identified as ethylamine hydrobromide (m.p. 159.5°) by a mixed melting point with an authentic sample.

[5] Kraus and Eatough added the lithium gradually to the ethylamine solution. On carrying out the reaction in such a manner we obtained the same results as with the procedure described here.

A red color developed as the reaction proceeded, but vanished on agitating the solution. No pressure developed during the reaction and the solution was entirely colorless when all the lithium had disappeared. The ethylamine was removed and the residue distilled. No gas was evolved during either of these operations. The distillate solidified in the receiver and melted at 41–45°. After purification, either by sublimation under vacuum or crystallization from pentane at −78°, the compound melted at 47–48° and gave no depression in melting point when mixed with authentic triphenyl-N-ethylaminosilane; yield 65–85%.

Concentration of Ether Solutions of "Triphenylsilicyl Ethylammine" and of Triphenyl-N-ethylaminosilane.—Solutions of both compounds in anhydrous ether were heated under reflux for one to three days under P_2O_5 drying tubes. On evaporation of the ether, the residues had the same melting points as the starting materials.

Hydrolysis of "Triphenylsilicyl Ethylammine" and of Triphenyl-N-ethylaminosilane.—Both compounds were heated several hours under reflux in a water–acetone mixture. On evaporation of the solvent, mixtures were obtained melting over a range corresponding to mixtures of triphenylsilanol and hexaphenyldisiloxane. By shaking the finely powdered material with ether, the more soluble silanol and some disiloxane dissolved leaving pure disiloxane, m.p. 223–225°, identified by mixed melting point.

Reaction of Ethylamine Hydrochloride with "Triphenylsilicyl Ethylamine" and with Triphenyl-N-ethylaminosilane.—In the vacuum reaction flask, ethylamine was condensed on a mixture of 2.5 g. (0.00825 mole) of triphenyl-N-ethylaminosilane and 0.61 g. (0.00825 mole) of ethylamine hydrochloride. The mixture was stirred three hours after complete solution had been effected. The solvent was removed and the residue distilled to yield 1.88 g. (73%) of triphenylchlorosilane, m.p. 96–97°, identified by mixed melting point. The same results were obtained with "triphenylsilicyl ethylammine."

Reaction of Lithium with "Triphenysilicyl Ethylammine" and with Triphenyl-N-ethylaminosilane.—Approximately 50 ml. of anhydrous ethylamine was condensed on 11 g. of "triphenylsilicyl ethylamine" and 0.25 g. (0.036 atom) of lithium in the vacuum reactor. A red solution was formed as the lithium dissolved without evolution of gas. The ethylamine was removed to a trap and anhydrous ammonia condensed on the tan residue. The material was not appreciably soluble in liquid ammonia. To the mixture was added 5.7 g. of bromobenzene. The bromobenzene solidified on coming in contact with the liquid ammonia and on warming went into solution. A deep brown solution and a light solid were obtained after four hours. The ammonia was removed and the residue distilled to give 4 g. (70%) of bromobenzene. The residue was removed from the vacuum line, shaken with anhydrous ether, and filtered. The insoluble material was inorganic and gave a strong lithium flame test. On evaporation, the ether extract gave a solid which still contained lithium salts. Several recrystallizations from low boiling petroleum ether gave a small amount of triphenylsilanol and large amounts of tar. The same results were obtained when triphenyl-N-ethylaminosilane was subjected to the same sequence of reactions.

In another run, the red ethylamine solution was treated directly with ethylamine hydrochloride. Removal of the solvent and distillation of the residue yielded diphenylbis-(ethylamino)-silane, b.p. 120–122° (1 mm.).

Anal. Calcd. for $C_{16}H_{22}N_2Si$: Si, 10.4; neut. equiv., 135. Found: Si, 10.2; neut. equiv., 139.

Reaction of Various Compounds with Lithium in Ethylamine.—A similar procedure was followed for all compounds studied. A weighed amount (always an excess) of lithium was introduced into the vacuum flask in which the reaction was to be carried out. To this was added a weighed sample of the organic compound under consideration. The method of adding the organic material varied with its physical nature. Solid materials were transferred directly into the reaction flask from the paper on which they were weighed. Non-volatile liquids were weighed in small vials and washed into the reaction flask with a small amount of anhydrous ether. The ether was then removed by opening the system to the vacuum pump. Volatile liquids were weighed in small vials which were then dropped into a vacuum flask attached to another part of the line. The entire system was then evacuated and the liquid transferred into the reaction flask by distillation.

Ethylamine was distilled into the flask, and the resulting mixture was stirred. In all cases where reaction occurred, a red color developed in the earlier stages. This was later masked by the blue color of dissolved lithium. When all the lithium had dissolved, the mixture was stirred an additional one to three hours. It was then treated with excess ethylamine hydrochloride, which hydrolyzed all organometallic compounds present and reacted with the excess lithium to evolve hydrogen. The pressure of the hydrogen was measured by means of an open-end manometer. From the ideal gas law, the number of moles of hydrogen was computed. From this followed the number of moles of excess lithium and thence the number that had been absorbed. Check runs were made. The results are summarized in Table I.

The Reaction of Triphenyl-N-ethylaminosilane with Lithium and Ethylamine Hydrochloride.—Anhydrous ethylamine was condensed on a mixture of 4.87 g. (0.016 mole) of triphenyl-N-ethylaminosilane, 1.31 g. (0.16 mole) of ethylamine hydrochloride and 0.112 g. (0.016 atom) of lithium. A transient red color developed on stirring. After 30 minutes the lithium was all consumed and the solution was colorless. No gas had been generated. The solvent was removed and the residue distilled to give 3.15 g. (65%) of triphenyl-N-ethylaminosilane, m.p. 47–48°, identified by mixed melting point.

The Reaction of Triphenylmethylsilane with Lithium and Ethylamine Hydrochloride.—Anhydrous ethylamine was condensed on a mixture of 4.11 g. (0.015 mole) of triphenylmethylsilane, 0.105 g. (0.015 atom) of lithium and 1.22 g. (0.015 mole) of ethylamine hydrochloride. On stirring the lithium went into solution, a transient red color developing. When the reaction was complete, the solution was colorless. From a pressure measurement, 0.0017 mole of gas had been liberated. The solvent was removed and the residue distilled to yield 3.2 g. (78%) of triphenylmethylsilane, m.p. 64–66°. One recrystallization from ethanol yielded 2.5 g. (61%) of the compound, m.p. 67.5–68.5°, identified by mixed melting point.

The Reaction of Triphenylbromosilane with Triphenyl-N-ethylaminosilane Polylithium.—Anhydrous ethylamine was condensed on a mixture of 0.70 g. (0.0023 mole) of triphenyl-N-ethylaminosilane and 0.094 g. (0.0134 atom) of lithium. The mixture was stirred until all the lithium was consumed. The resulting red solution was treated with 4.54 g. (0.0134 mole) of triphenylbromosilane. The red color disappeared without the evolution of a gas. The solvent was removed and the residue distilled to yield a semi-solid material which on crystallization from pentane at −78° gave 1.17 g. of triphenyl-N-ethylaminosilane, m.p. 47–48°, identified by mixed melting point. Obviously an additional 0.47 g. of triphenyl-N-ethylaminosilane was formed in this reaction.

Acknowledgment.—The authors gratefully acknowledge Research Corporation and the Purdue Research Foundation whose financial assistance made this work possible.

LAFAYETTE, INDIANA