

$(C_6H_5)_3Si-C_2H_5NH_2 + LiBr$. Triphenylsilyl ethylamine 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 triphenylsilyl. The latter compound reacts with ammonium bromide to form triphenylsilylamine and with phenyl bromide to form tetraphenylsilyl.

On treating lithium triphenylsilyl with trimethyltin chloride in liquid ammonia solution, the triphenylsilyl 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 triphenylsilyl bromide and trimethyltin bromide.

Triphenylsilyl ethylamine 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 triphenylsilyl group with a molecule of ethylamine.

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The Reactions of Sodium Triphenylstannide with Polyhalogenated Methanes

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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 Nutting² 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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(2) Kraus and Nutting, *THIS JOURNAL*, **64**, 1622 (1932).

derivatives were obtained. Kraus and Neal³ have studied the reaction of sodium trimethylstannide with methylene chloride and with chloroform. With methylene chloride, the stannyl groups are substituted for the halogens, but with chloroform a more complicated reaction occurs in which trimethyltin is formed and an unsaturated methylenic carbon linkage results. With carbon tetrachloride, all the tin was recovered as trimethyltin and the halogen as sodium chloride, but what happened to the carbon was not determined. Similarly, in treating carbon tetrachloride with sodium triphenylgermanide, Kraus and Nutting failed to find what happened to the carbon atom.

It seemed of interest to study the reaction of sodium triphenylstannide with the same series of halogenated methanes. In the case of both methylene chloride and chloroform, triphenylstannyl groups were substituted for the halogens, di-triphenylstannylmethane and tri-triphenylstannylmethane being obtained as products of reaction. In the case of carbon tetrachloride, however, practically all the tin was recovered as triphenyltin and the halogen as sodium chloride. No gases were evolved and it was not obvious what became of the carbon atom in this reaction.

It is evident that reactions of compounds of the type MA_3R_3 with the poly-halogenated methanes are greatly influenced by the nature of the substituent groups R.

Experimental

The experimental procedure was much the same as that already described by Kraus and Nutting in connection with their investigation of the reactions of sodium triphenylgermanide. Triphenyltin was treated with sodium in liquid ammonia in equivalent amount and the organic halide was added to the solution. Reaction took place readily and the resulting products were separated from the residue after the evaporation of ammonia by means of suitable solvents.

Di-triphenylstannylmethane.—The product of reaction of sodium triphenylstannide with methylene chloride was extracted with benzene and the residue obtained on distillation of the solvent and removal of the last traces of benzene by means of a pump was recrystallized from hot petroleum ether. The final product melted at 104.5° (corr.).

The tin content of the compound was determined as stannic oxide in the usual way by oxidation with fuming sulfuric and nitric acids in a weighed Pyrex test-tube.

Anal. Calcd. for $[(C_6H_5)_3Sn]_2CH_2$: Sn, 34.73; mol. wt., 713.8. Found: Sn, 34.63, 34.67; mol. wt., 743, 732.

The molecular weight of the compound was determined cryoscopically in benzene.

Di-triphenylstannylmethane is a white, crystalline solid which melts at 104.5°. It is very soluble in benzene, ether, chloroform and trichloroethylene. It is soluble in hot petroleum ether but only slightly soluble in the cold ether. It is best recrystallized from petroleum ether solution, evaporating slowly at 50°.

Tri-triphenylstannylmethane.—Sodium triphenylstannide was treated with an equivalent quantity of chloroform and, on completion of the reaction and evaporation of the solvent, the residue was extracted with benzene. The benzene extract was distilled, the last traces of solvent were evaporated on a steam-bath, and the product was recryst-

(3) Kraus and Neal, *THIS JOURNAL*, **52**, 4426 (1930).

tallized from petroleum ether. The final product melted at 128° (corr.). A very small quantity of triphenyltin was recovered in this reaction and identified by its melting point, 231°. The tin content of the compound was determined as SnO₂ in the usual way.

Anal. Calcd. for [(C₆H₅)₃Sn]₃CH: Sn, 33.51. Found: Sn, 33.47, 33.49, 33.46.

The molecular weight of the compound was determined cryoscopically in benzene. Calcd. for [(C₆H₅)₃Sn]₃CH: mol. wt., 1063. Found: mol. wt., 1040, 1070, 1040.

Tri-triphenylstannylmethane is a white, crystalline solid melting at 128°. It is very soluble in benzene, ether, chloroform and trichloroethylene. It is soluble in hot petroleum ether but only slightly soluble in the cold ether. It is sparingly soluble in alcohol and insoluble in water and liquid ammonia. It is best recrystallized from petroleum ether, evaporating under reduced pressure.

Reaction with Carbon Tetrachloride.—Carbon tetrachloride was found to react readily with sodium triphenylstannide in liquid ammonia. The residue remaining in the reaction tube, after evaporation of ammonia, was extracted with benzene and from this was obtained triphenyltin and a very small amount of material that failed to melt at 360° and which carbonized on heating in a flame. The main product of the reaction was triphenyltin which was identified by its melting point and by analysis. In two reactions there were obtained 0.5794 and 0.5818 g. of sodium chloride, respectively, as against 0.5846 g. required according to the amount of material used. No gases were given off in the course of the reaction and no product could be found indicating what became of the carbon atom of the carbon tetrachloride.

Summary

Di-triphenylstannylmethane and tri-triphenylstannylmethane have been prepared by the action of sodium triphenylstannide on methylene chloride and chloroform, respectively, in liquid ammonia. The corresponding quaternary derivative was not obtained with carbon tetrachloride.

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The Pyrolysis of *n*-Butane at Low Decomposition Temperatures

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In the preceding paper¹ it was mentioned that Norris and co-workers studied the pyrolysis of paraffin hydrocarbons at incipient decomposition temperatures and stated that under these conditions the breakdown of the molecule occurred at a specific C-C location. This is in contrast to the results of earlier investigators who, however, employed higher temperatures. In these higher temperature studies, the results pointed to scission at several places in the molecule rather than at an exclusive location although differences in the strengths of the various C-C bonds were evident. It became a matter of importance, therefore, to check Norris' results for they seemed to indicate that this slight difference in the strength of C-C bonds could be capitalized if low enough decomposition temperatures were used.

(1) Hurd and Pilgrim, *THIS JOURNAL*, **55**, 4902 (1933).