tion,[12] they may be only slightly operative on the polarization properties as in the present case.

It should be recalled, however, that also the [Ni(Me_6tren)Br]Br complex, in which the nickel ion is in a C_3 site symmetry, has a value of only 3.4 BM.[2] This has not been explained although a dynamical Jahn-Teller distorsion, as so often invoked for copper complexes,[13] could account for it.

Acknowledgments.—Thanks are expressed to Professor L. Sacconi for interest and to D. Masi for X-ray technical assistance.

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Reactions of Hexachlorocyclotriphosphazene with Triphenylstannyl- and Tri-*n*-butylstannyllithium

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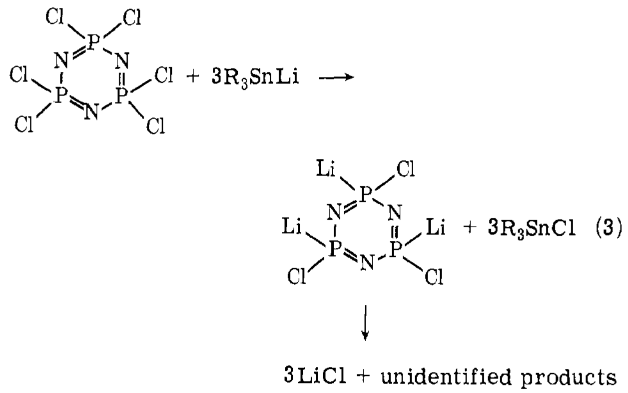
Hexachlorocyclotriphosphazene has been previously shown to undergo nucleophilic substitution reactions with hydroxides, alkoxides, phenoxides, alcohols, many sulfur-containing organic compounds, primary or secondary amines, ammonia, hydrazine, organometallic reagents, and metal salts to give the corresponding partially or fully substituted derivatives. We now wish to report the results of the reactions of hexachlorocyclotriphosphazene with triphenylstannyllithium and tri-*n*-butylstannyllithium, aimed at the synthesis of fully substituted phosphazene derivatives of the type $[NP(SnR_3)_2]_3$, where R = C_6H_5 or *n*-C_4H_9. We had thought that the chlorine atoms on the chlorophosphazene would undergo simple nucleophilic substitution by triphenylstannyl or tri-*n*-butylstannyl groups to yield the corresponding phosphazene derivatives in accordance with the equations

$$[PNCl_2]_3 + 6(C_6H_5)_3SnLi \longrightarrow [NP(Sn(C_6H_5)_3)_2]_3 + 6LiCl \quad (1)$$

$$[PNCl_2]_3 + 6(n\text{-}C_4H_9)_3SnLi \longrightarrow [NP(Sn(n\text{-}C_4H_9)_3)_2]_3 + 6LiCl \quad (2)$$

Instead we have found that the chlorophosphazene reacts with $(C_6H_5)_3SnLi$ and $(n\text{-}C_4H_9)_3SnLi$ in an unusual manner which involves breaking the phosphazene ring with the production of hexaphenyldistannane and hexa-*n*-butyldistannane, respectively, in good yields. Lithium chloride and a complex solid containing carbon, hydrogen, tin, phosphorus, and nitrogen are also obtained. This solid which appears to be impure has not been identified. No partially or fully substituted phosphazene derivatives containing $(C_6H_5)_3Sn$ or $(n\text{-}C_4H_9)_3Sn$ groups were obtained from the products of these reactions.

A reasonable reaction scheme which would account for the formation of the distannanes involves the following sequence of reactions



$$3R_3SnLi + 3R_3SnCl \longrightarrow 3R_3SnSnR_3 + 3LiCl$$

where R = C_6H_5 or *n*-C_4H_9. This reaction sequence must, of course, be regarded as tentative. A comparison, however, of the bond dissociation energies of P–Sn (44 kcal/mmol) and P–Li (64 kcal/mmol) would support the postulation of reaction 3.[1] The possibility that R_3SnSnR_3 may be present as a contaminant in the starting materials (R_3SnCl) and/or results as a byproduct from the reaction of R_3SnCl and lithium due to incomplete formation of R_3SnLi has been considered. If so, it can only be present in trace amounts since the conversion to R_3SnLi is usually nearly quantitative. However, it is well known that the Sn–Sn bond in both hexa-*n*-butyldistannane and hexaphenyldistannane is readily cleaved by lithium metal in tetrahydrofuran.[2,3]

The fact that high yields of R_3SnSnR_3 compound are obtained and that an excess of lithium metal was used to ensure complete conversion of R_3SnCl to R_3SnLi should make very improbable the formation of R_3SnSnR_3 from R_3SnCl and lithium in the absence of hexachlorocyclotriphosphazene. Furthermore, the fact that all the chlorophosphazene was consumed would also support the reaction path proposed since it is very improbable that R_3SnSnR_3 would react with the phosphazene trimer.

The results obtained in this study are in general agreement with some earlier observations of anomalous results from attempted arylations or alkylations of chlorocyclophosphazenes. Reactions with some metal organic compounds have been shown to result in ring cleavage of the chlorocyclophosphazenes at rates which are comparable with, or faster than, rates of alkylation of the cyclic compounds. Bezman and Reed[4] studied the reactions of hexachlorocyclotriphosphazene with sodium salts of some carboxylic acids. They have shown that the reaction with the sodium salt of benzoic acid results in the production of benzonitrile, benzoic anhydride, sodium chloride, and some phosphorus-containing compounds whose identity could not be established conclusively. The P–N ring probably undergoes rupture.[4] In contrast to hexachlorocyclotriphosphazene, hexafluorocyclotriphosphazene has been reported to undergo smooth reactions with the

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(1) The bond energies were calculated using the equation $D_{A-B} = {}^1/_2 \cdot (D_{A-A} + D_{B-B}) + 23.06(X_A - X_A)^2$.

(2) C. Tamborski, F. E. Ford, and E. J. Soloski, *J. Org. Chem.*, **28**, 237 (1963).

(3) H. Gilman, O. L. Mars, and S.-Y. Sim, *ibid.*, **27**, 4232 (1962).

(4) I. I. Bezman and W. R. Reed, *J. Amer. Chem. Soc.*, **82**, 2167 (1960).

organolithium reagents yielding partially and fully substituted phosphazenes.[5]

Experimental Section

Materials.—Reagent grade tetrahydrofuran used in these experiments was refluxed with calcium hydride, distilled, and stored over calcium hydride. Triphenyltin chloride and tri-*n*-butyltin chloride were obtained from Metal and Thermit Corp. and used as received. The hexachlorocyclotriphosphazene was prepared from the NH_4Cl–PCl_5 reaction in monochlorobenzene; mp 111–112° (lit.[4] mp 114°). Mol wt: calcd, 348; found, 350 in benzene. *Anal.* Calcd for $[PNCl_2]_3$: N, 12.06; P, 26.72; Cl, 61.20. Found: N, 12.03; P, 26.85; Cl, 61.04. The infrared spectrum is consistent with that of hexachlorocyclotriphosphazene reported in the literature. Triphenylstannyllithium and tri-*n*-butylstannyllithium were prepared by the method of Gilman, *et al.*[3,6]

Analyses.—Elemental analyses and molecular weight determinations were carried out by Galbraith Microanalytical Laboratories, Inc., Knoxville, Tenn. The infrared spectra (listed in Table I) were obtained with a Beckman IR-10 spectrophotometer. The spectra of liquids were determined on thin films supported by KBr plates. The spectra of solids were determined using KBr pellets. Melting points were obtained using Pyrex capillaries on a Thomas-Hoover capillary melting point apparatus and are reported uncorrected. The ^1H nmr spectra were recorded with a Varian Model A-60A nuclear magnetic resonance spectrometer.

TABLE I

INFRARED SPECTRAL DATA (CM^{-1})[a]

$(C_6H_5)_3SnSn(C_6H_5)_3$, KBr disk

3060 (m), 3000 (w), 2920 (w), 1870 (w), 1820 (w), 1730 (w), 1640 (w), 1575 (w), 1160 (w), 1075 (s), 1025 (m), 1000 (s), 970 (vw), 730 (vs), 700 (vs), 675 (vw), 660 (w), 445 (s)

$(n\text{-}C_4H_9)_3SnSn(n\text{-}C_4H_9)_3$, neat

2835 (b, vs), 1450 (vs), 1420 (sh), 1380 (m), 1340 (sh), 1290 (sh), 1255 (s), 1200–970 (vb, vs), 960 (sh), 860 (s), 790 (vs), 655 (vs), 640 (m), 580 (vs), 485 (vs)

[a] Key: v, very; s, strong; m, medium; b, broad; w, weak.

Reaction of Triphenylstannyllithium with Hexachlorocyclotriphosphazene.—Triphenyltin chloride (22.5 mmol) was dissolved in 30 ml of dry tetrahydrofuran and the solution was added to 0.53 g (76 mg-atoms) of lithium metal cut into small pieces and suspended in 2 ml of dry tetrahydrofuran. The reaction mixture was stirred for 6 hr at room temperature under a dry nitrogen atmosphere. The insoluble matter was removed by passing the contents through a glass wool plug. The solution was transferred to a 100-ml, three-necked, round-bottomed flask equipped with a reflux condenser and a nitrogen inlet tube. A solution of hexachlorocyclotriphosphazene (3.28 mmol) in 40 ml of dry tetrahydrofuran was slowly added to the green solution of $(C_6H_5)_3SnLi$. After being stirred for 12 hr at room temperature, the mixture was refluxed for another 8 hr. Tetrahydrofuran was stripped off under vacuum leaving a tan solid in the flask. The solid was boiled with 60 ml of ether. The ether solution yielded 0.34 g of a white solid which melted at 190–220°. The infrared and ^1H nmr spectra of this solid were similar to those of the solid obtained from benzene solution and later identified as hexaphenyldistannane. The ether-insoluble solid was boiled with 50 ml of petroleum ether (bp 30–60°). A white solid (0.03 g) melting at 230–231° was recovered from the solution. This solid was identified as hexaphenyldistannane by its infrared spectrum and melting point. Recrystallization of the petroleum ether insoluble solid residue from hot benzene gave 5.22 g of a white, crystalline solid, mp 235–236° (lit.[7] mp 232°). Mol wt: calcd, 699; found, 690 in benzene. *Anal.* Calcd for $(C_6H_5)_3SnSn(C_6H_5)_3$: C, 61.77; H, 4.29; Sn, 33.94. Found: C, 61.52; H, 4.41; Sn, 33.67.

The ^1H nmr spectrum in completely deuterated chloroform showed a complex peak at 2.63 ppm (tetramethylsilane used as internal standard) which falls in the aromatic region. The total yield of hexaphenyldistannane was 5.59 g or 71% of theory.

The benzene-soluble solid was extracted with boiling tetrahydrofuran. Evaporation of the solvent yielded 1.17 g of a solid shown by its chloride content and its flame color to contain mostly lithium chloride.

The small amounts of a white residue insoluble in boiling tetrahydrofuran did not yield to further attempts at separation and identification.

Reaction of Tri-*n*-butylstannyllithium with Hexachlorocyclotriphosphazene.—Tri-*n*-butyltin chloride (20.0 mmol) was added to lithium metal (100 mg-atoms) cut into very small pieces and suspended in 2 ml of tetrahydrofuran. A dry nitrogen atmosphere was maintained. The reaction was initiated by adding a tiny crystal of iodine and warming the reaction mixture. Forty milliliters of tetrahydrofuran was slowly added to the reaction flask. The contents was stirred for 4 hr at room temperature and the reaction mixture was occasionally warmed. The insoluble matter was removed by passing the contents through a glass wool plug. The yellow solution containing $(n\text{-}C_4H_9)_3SnLi$ was transferred to a 100-ml, three-necked, round-bottomed flask fitted with a reflux condenser and nitrogen-inlet tube. Hexachlorocyclotriphosphazene (2.57 mmol) dissolved in 30 ml of tetrahydrofuran was slowly added to the yellow solution of the lithium salt. The reaction mixture was continuously stirred overnight and then refluxed for 8 hr. The white solid was then filtered, washed with tetrahydrofuran, and dried; yield 0.05 g. This solid was identified as LiCl by its chloride content and flame test.

Tetrahydrofuran was removed from the filtrate under vacuum leaving a greasy, yellowish residue, together with some liquid. The residue was extracted with 60 ml of boiling ether. Evaporation of the ether gave 3.3 g of a colorless liquid. Fractionation of this liquid at 0.2 mm and at a bath temperature of 150° yielded 0.61 g of a colorless liquid distilling at 106–108°. The infrared and H nmr spectra of this liquid were similar to those of the liquid obtained as the second fraction and identified as hexa-*n*-butyldistannane. The poor analytical data obtained for this material, however, indicate that this material was impure.

The bath temperature was raised to 230°. A liquid distilling at 152–154° (0.025 mm) was collected; yield 2.29 g, 49%. The boiling point reported in the literature for hexa-*n*-butyldistannane is 156–160° (0.025 mm).[8] Mol wt: calcd, 579; found, 560 in benzene (vapor phase osmometry). *Anal.* Calcd for $(n\text{-}C_4H_9)_3SnSn(n\text{-}C_4H_9)_3$: C, 49.70; H, 9.31; Sn, 40.97. Found: C, 47.89; H, 9.36; Sn, 42.93. The general observation that, in the combustion method, analysis for carbon in organotin compounds commonly gives low results because of the retention of some CO_2 by the SnO_2 residue accounts for the rather low carbon and rather high tin analyses obtained for hexa-*n*-butyldistannane.[9]

The ether-insoluble residue was extracted several times with boiling tetrahydrofuran. Evaporation of tetrahydrofuran yielded 0.88 g of a white solid identified as lithium chloride by its chloride analysis and flame test.

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Preparation and Characterization of Oxobis(fluorosulfato)cerium(IV) and Trifluoro(fluorosulfato)cerium(IV)

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Peroxydisulfuryl difluoride has been reported to react with transition metal carbonates yielding oxyfluorosulfates in the higher oxidation state.[1] Bromine(I) fluorosulfate has been reported as an efficient fluoro-

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