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The Reaction of Phosphorus Pentafluoride and Tetraalkyltin Compounds

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Alkyltetrafluorophosphoranes can be prepared in good yield by the room temperature reaction of phosphorus pentafluoride and tetraalkyltin compounds. Careful investigation of the stoichiometry of this reaction indicates that this reaction is not as straightforward as one might expect, however. In all of the reactions attempted some of the phosphorus was retained in the nonvolatile residue of the reaction. Evidence is presented which indicates that this residue contains a complex of the formula R_3SnPF_6, whose structure is probably similar to other known compounds R_3SnX ($X = ClO_4$, BF_4, AsF_6, and SbF_6).

Alkyltetrafluorophosphoranes have been synthesized by a number of different methods. The method described recently by Schmutzler[1] involving fluorination of alkylchlorophosphines with arsenic or antimony trifluorides is probably the easiest reaction for such a synthesis and moreover can be used for preparation of other compounds of the formula R_nPF_{5-n}.

We wish to report here the synthesis of alkyltetrafluorophosphoranes in good yield from the direct reaction of tetraalkyltin compounds and phosphorus pentafluoride. Handling of these reactants and the products is easily accomplished in a high vacuum system of standard design. This reaction has the further advantage that the reactants are commercially available, thus eliminating the difficulties involved in preparation of alkylchlorophosphines and alkylchlorophosphoranes.

Experimental

All manipulations were carried out using a standard high vacuum system. Tetraalkyltin compounds and trimethyltin chloride were purchased from Metal and Thermite Co., Rahway, N. J., and used without further purification. Phosphorus pentafluoride was obtained from the Matheson Co. This material was purified before use by repeated vacuum line fractionation through −112 and −196° traps. The small quantity of POF_3 always present collected in the −112° trap; phosphorus pentafluoride, shown by its infrared spectrum[2,3] to be free of POF_3, was collected in the −196° trap.

Infrared spectra of gases were run in 10-cm. cells with sodium chloride windows; spectra of solids were run as Nujol mulls. Routine spectra were recorded on a Beckman IR-10 grating spectrometer. Several higher resolution spectra were also run on a Perkin-Elmer Model 421 infrared spectrometer. Infrared absorptions for the gaseous alkyltetrafluorophosphoranes, not previously listed in the chemical literature, are recorded in Table I.

Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

The Reaction of Tetramethyltin and Phosphorus Pentafluoride.—A 500-ml. Pyrex bulb fitted with a side arm was evacuated, heated with a Bunsen flame to remove the remaining traces of moisture, and then filled with 17.8 mmoles of phosphorus pentafluoride and 2.998 g. (16.8 mmoles) of tetramethyltin. The tetramethyltin was weighed in a container fitted with a stopcock and then transferred to the bulb by means of the vacuum line. The bulb was sealed off and left at room temperature. A white solid formed immediately upon warming from −196°. After 24 hr. the reaction bulb was again attached to the line *via* a tube-opening device. The volatile contents were passed through −64, −96, and −196° traps with the contents of each trap then being recycled several times. Infrared spectra run in a 10-cm. gas cell at pressures of 7 to 9 mm. were used to identify fractions and to help judge the extent of fractionation. The −196° trap collected 12.8 mmoles of PF_5. The −96° trap collected 3.3 mmoles of the product CH_3PF_4, and the −64° trap collected 2.174 g. (12.2 mmoles) of tetramethyltin. This indicates an over-all conversion to CH_3PF_4 of 19%. Only 90% of the original phosphorus can be accounted for as volatile phosphorus fluorides.

With a similar bulb containing 15.5 mmoles of PF_5 and 2.9910 g. (16.7 mmoles) of tetramethyltin left at room temperature for 1 week, 3.0 mmoles of PF_5, 8.5 mmoles of CH_3PF_4, and 1.4896 g. (8.3 mmoles) of tetramethyltin were found. Here the over-all conversion to CH_3PF_4 was 55% and only 74% of the original phosphorus can be accounted for as volatile phosphorus fluorides.

The product collected in the −96° trap was purified by recycling through −64, −96, and −196° traps, and a gas phase molecular weight determination was made using a bulb of calibrated volume with sample pressures ranging from 100 to 300 mm.; temperature 24.1°. The results indicated the presence of a small amount of tetramethyltin. Further fractionations led to progressively lower values until a limiting value of 122.8 ± 0.7 was reached (calcd. for CH_3PF_4 122.0).

Sixteen separate experiments of the type above were carried out, varying molar ratios and length of reaction period. The results of some of these experiments, illustrating variations in reaction time and ratio of reactants, are tabulated in Table II. In all runs a 65 ± 8% yield of CH_3PF_4 was obtained, if unreacted PF_5 was accounted for in this calculation. In each reaction some of the phosphorus (usually about 20%) was retained in the bulb in the nonvolatile residue.

The white solid remaining in the reaction bulb when exposed to air slowly etched the glass. It fumed vigorously when water was dropped into the bulb and only partially dissolved in water, leaving a highly acidic solution. The water-insoluble product was identified as trimethyltin fluoride by elemental analysis and infrared spectra.

Anal. Calcd. for C_3H_9SnF: C, 19.72; H, 4.96; F, 10.39. Found: C, 19.83; H, 5.00; F, 10.56.

An infrared spectrum of the solid reaction product was obtained by sealing the bulb after removal of the volatile products and reopening it in a nitrogen-flushed dry bag. Reproducible Nujol mulls of the solid could be prepared in these anhydrous conditions if spectra were taken within a few hours; some hydrolysis products could be observed over a more extended period of time. Infrared spectra were also taken of the white solid after it had been exposed to the air for 2 weeks. The observed infrared bands for these substances and also for trimethyltin fluoride are listed below.

The solid residue showed bands at 1413 (w), 1290 (w, br), 1208 (w), 1195 (w, sh), 975 (s), 840 (s, sh), 805 (s), 742 (s), 557 (s), 445 (s), 260 (w) cm.$^{-1}$.

Intermediate hydrolysis showed new bands appearing at 1285,

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[1] R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964). Other methods of synthesis for these compounds are referenced in this paper.

[2] J. P. Pemsler and W. G. Planet, *J. Chem. Phys.*, **24**, 920 (1956).

[3] H. S. Gutowsky and A. D. Liehr, *ibid.*, **20**, 1652 (1952).

TABLE I

INFRARED ABSORPTION PEAKS OF ALKYLFLUOROPHOSPHORANES (CM.$^{-1}$)[a]

CH_3PF_4			$CH_3CH_2PF_4$			$CH_2{=}CHPF_4$			n-$CH_3CH_2CH_2PF_4$		
	6 mm.	48 mm.		7 mm.	55 mm.		7 mm.	46 mm.		8 mm.	44 mm.
						705	w				
835	s		840	vs		845	vs		833	vs	
									855	ms	
			900	vs		908	vs				
930	s								922	s	
			950	s		970	vs		960	vs	
						1055	w	s	1070	m	
1008	s		1025	m							
						1090		w, sh			
						1140		w			
									1215	w	w, sh
			1270	w	m	1274		w			
			1285		m, sh	1285		w	1252	w	m
						1295		w, sh			
									1320		w, sh
1320	w	s				1360		w	1355	w	m
1330	w	s									
1335											
						1398	m	vs	1395	w	m
			1420		m, sh						
						1401	m	vs			
1435		w	1430	w	m	1413	m	vs	1430		m
1445		w, sh	1470	w	m	1465		w	1470	w	ms
						1618		w			
						1626	vw	w			
						1634		m			
						1644		w			
2930		w	2910	w	m	2930		w	2895	w	
2995		w	2970	w	m	2990		w	2950	w	
3060		w	3000	w	s	3055	vw	w	2985	m	

[a] Spectra of these gaseous species were taken in a gas cell of 10-cm. path length with NaCl plates, using a Beckman IR-10 spectrometer. Several of the compounds were also observed using a Perkin-Elmer Model 421 spectrometer. In these spectra some further structure was observed on the P–F absorptions.

TABLE II

DATA FOR THE REACTION OF TETRAMETHYLTIN AND PHOSPHORUS PENTAFLUORIDE[a]

Run number	I	II	III	IV	V	VI	VII	VIII	IX
Time of reaction	24 hr.	48 hr.	5 days	1 week	2 weeks	4 weeks	1 week	24 hr.	4 days
PF_5, mmoles									
Original	17.8	16.0	17.3	15.5	15.4	14.9	15.2	25.6	26.1
Recovered	12.8	11.8	7.4	3.0	2.9	$<.2$	2.4	18.0	12.3
Used	5.0	4.2	9.9	12.5	12.5	14.7	12.8	7.6	13.8
Methyltetrafluorophosphorane, mmoles	3.3	2.4	6.8	8.5	8.6	10.2	8.4	4.6	9.9
% conversion[b]	67	57	69	68	69	69	66	61	72
Over-all % yield	19	15	39	55	56	69	55	18	38
% P found[c]	90	89	82	74	75	70	71	88	85
Tetramethyltin, mmoles									
Original	16.8	16.1	17.2	16.7	16.2	14.2	29.6	13.2	13.3
Recovered	12.2	12.4	9.1	8.3	6.2	4.4	20.4	8.0	3.7
Used	4.6	3.7	8.1	8.4	10.0	9.8	9.2	5.2	9.6

[a] Values given in mmoles. [b] Calculated as [mmoles of CH_3PF_4/mmoles of PF_5 used] × 100. [c] Calculated as [mmoles of PF_5 recovered plus mmoles of CH_3PF_4/mmoles of PF_5 originally present] × 100.

1155, and 512 cm.$^{-1}$, while the bands in the 800 cm.$^{-1}$ region coalesced and the 445 cm.$^{-1}$ band moved down to a broad peak around 360 cm.$^{-1}$.

The solid residue after standing 2 weeks in air showed bands at 1320 (m, sh), 1295 (s), 1270 (m, sh), 1215 (w), 1194 (w), 1155 (s), 910 (w), 875 (w), 815 (sh), 778 (m, br), 722 (w), 555 (s), 515 (w, sh), 495 (mw), 360 (m, br) cm.$^{-1}$.

Trimethyltin fluoride[4] showed bonds at 1412 (w), 1216 (w), 1194 (w), 782 (s), 555 (s) cm.$^{-1}$.

The Reaction of Ammonia and the Solid Formed in the Tetramethyltin–Phosphorus Pentafluoride Reaction.—After pumping on the solid reaction product prepared in one of the reactions of tetramethyltin and phosphorus pentafluoride (run No. VI, Table II) for 0.5 hr., 22.2 mmoles of anhydrous ammonia was condensed into the bulb. The bulb was closed off from the vacuum system and brought to room temperature. After 3 hr. 11.8 mmoles of unreacted ammonia was collected. The following day an additional 0.4 mmole was pumped off. The white solid was removed from the bulb. It did not appear to react with air and left a white solid when dissolved in water. This latter solid was filtered and dried for several hours under vacuum; its infrared spectrum showed it to be trimethyltin fluoride. On addition of an aqueous solution of tetraphenylarsonium chloride to

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[4] R. Okawara, D. Webster, and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960).

the filtrate, a white, finely divided precipitate formed. This was filtered and dried. Infrared spectra of the original solid residue and this latter precipitate were run using Nujol mulls and CsI optics. Comparison with the known spectrum[5] of $(CH_3)_3Sn(NH_3)_2^+ClO_4^-$ and knowledge of the approximate positions of bands due to perchlorate and hexafluorophosphate ions led us to conclude that the original solid was a mixture of trimethyltin fluoride and the salt $(CH_3)_3Sn(NH_3)_2^+PF_6^-$. The precipitate obtained on tetraphenylarsonium chloride addition was $(C_6H_5)_4As^+PF_6^-$.

Anal. Calcd. for $C_{24}H_{20}AsPF_6$: C, 54.36; H, 3.82; F, 21.58. Found: C, 54.37; H, 3.92; F, 21.69.

Infrared bands were observed for the original solid at 3398 (s), 3306 (m), 3208 (w), 1615 (ms), 1209 (s, sh), 1194 (s), 878 (s, sh), 818 (vs, br), 780 (sh), 593 (m), 555 (s), 368 (m, br), 328 (w, sh), 271 (w) cm.$^{-1}$.

Infrared bands of $(CH_3)_3Sn(NH_3)_2^+ClO_4^-$ were observed at 3350 (s), 3260 (s), 3200 (w), 2990 (w), 2900 (w), 1610 (m), 1425 (m), 1240 (s), 1222 (s), 1207 (s), 1100–1075 (s, br), 935 (w), 792 (s), 625 (s), 551 (m), 490 (w, sh), 441 (w) cm.$^{-1}$. The 1100–1075 and the 935 cm.$^{-1}$ absorption are due to the perchlorate ion.[5] The PF_6^- ion shows maxima at 845 and 559 cm.$^{-1}$.[6]

Infrared bands of $(C_6H_5)_4As^+PF_6^-$ were observed at 1485 (m), 1445 (s), 1315 (w), 1192 (w), 1085 (m), 1025 (w), 998 (w), 927 (w), 918 (w, sh), 858 (s), 838 (s), 822 (s), 743 (s), 725 (w, sh), 688 (m), 560 (m), 478 (w), 460 (w), 348 (w) cm.$^{-1}$.

Tetraethyltin and Phosphorus Pentafluoride.—Following a similar procedure, 5.2 g. (22.1 mmoles) of tetraethyltin was placed in a 500-ml. bulb, and the bulb was attached to the vacuum system and 21.8 mmoles of PF_5 added. The bulb was sealed and left for 26 days. White crystals formed slowly along with a dark brown oil. The volatile products were then fractionated on the vacuum line through the series of cold traps at −22.5, −78, −96, and −196°. Less than 1 mmole collected in the −196° trap. A total of 12.4 mmoles of POF_3 and product collected in the −112 and −78° traps. The tetraethyltin was stopped at −22.5°. By careful refractionation 10.9 mmoles of product was collected at −78° (50% yield). Purity was ascertained by a molecular weight determination at 143 mm. pressure and 22.7°; found 135.3, calcd. for $C_2H_5PF_4$ 136.0. The total of 13.4 mmoles of volatile phosphorus-containing compounds accounts for 61% of the original phosphorus in the sample.

The nonvolatile materials completely dissolved in ether. Two immiscible layers formed. One contained tetraethyltin and the second, brown in color, upon evaporation gave white crystals. This solid was recrystallized from methanol and shown by elemental analysis to be triethyltin fluoride. In other reactions no brown oil was observed. The white solid product fumed when water or methanol was added to the reaction bulb.

Anal. Calcd. for $C_6H_{15}SnF$: C, 32.05; H, 6.73; F, 8.45. Found: C, 32.13; H, 6.74; F, 8.32.

The Reaction of Tetravinyltin and Phosphorus Pentafluoride.—The reaction between 4.04 g. (18 mmoles) of tetravinyltin and 17.7 mmoles of PF_5 started immediately upon warming from −196°. Along with a colorless liquid, a brownish red oil and colorless crystals appeared. After 24 hr. at room temperature the volatile components were fractionated on the vacuum line through −78, −96, −112, and −196° traps. Approximately 4.5 mmoles (26% yield) of the product $CH_2{=}CHPF_4$ was finally collected in the −96 and −112° fractions. Gas phase molecular weight determined at 176 mm. pressure and 22.8°, 133.0; calcd. for $C_2H_3PF_4$, 134.0.

The Reaction of Tetra-*n*-propyltin and Phosphorus Pentafluoride.—After 18 days 14 mmoles of tetra-*n*-propyltin and 13.5 mmoles of PF_5 in a 1-l. reaction bulb at room temperature gave only 0.4 mmole of product. When heated further for 7 days at 60°, 3.2 mmoles (27% over-all yield) of propyltetrafluorophosphorane was collected in the −96° fraction. Gas phase molecular weight determined at 100 mm. pressure and 22.7°, 147.6; calcd. for $C_3H_7PF_4$, 150.1.

The Reaction of Tetramethyltin and Methyltetrafluorophosphorane.—A carefully dried 500-cc. Pyrex bulb with a side arm was evacuated and filled with 3.4037 g. (19.03 mmoles) of tetramethyltin and 27.5 mmoles of methyltetrafluorophosphorane. The bulb was sealed off and after no reaction had been determined to occur at room temperature, the bulb was placed in an 88° oven for 5 days. A small amount of brown oil formed but almost quantitative recovery of the reactants showed no reaction had occurred.

The Reaction of Trimethyltin Fluoride and Phosphorus Pentafluoride.—Trimethyltin fluoride was prepared by the addition of a solution of potassium fluoride to trimethyltin chloride dissolved in water. The solution was filtered and the solid dried at room temperature under vacuum for 15 hr. to remove any water retained by the sample. Trimethyltin fluoride (1.3 g., 7.1 mmoles) was placed in a 250-ml. Pyrex bulb fitted with a side arm. The bulb was evacuated and heated gently with a Bunsen flame. Then 7.0 mmoles of PF_5 was condensed into the bulb, which was sealed and allowed to stand at room temperature overnight. The bulb was connected to the vacuum line, and the volatile contents were fractionated through −64, −96, and −196° traps. Phosphorus pentafluoride (5.9 mmoles) collected at −196°. The −96 and −64° traps collected 0.4 mmole of unidentified products. After further pumping on the remaining solid the bulb was removed from the line and water added. The addition of water was accompanied by some fuming. A white solid remained. The water solution was highly acidic.

During the second run in which the only volatile components recovered were phosphorus pentafluoride and POF_3, anhydrous ammonia was added to the remaining solid in the bulb. The resulting white solid was treated as before, with partial dissolution in water followed by the addition of tetraphenylarsonium chloride solution to the filtrate. The infrared spectra of the original solid, the water-insoluble portion, and the tetraphenylarsonium salt correspond exactly to those found under similar treatment of the solid of the tetramethyltin–phosphorus pentafluoride reaction.

Discussion

In general the reaction $MR + M'X \rightarrow MX + M'R$ will proceed if the element M is more electropositive than the element M′. Hence tetraalkyltin compounds can serve as alkylating agents for a variety of elements. For example, tetraalkyltin compounds and boron halides react readily to give alkylboron dihalides or dialkylboron halides.[7]

The possibility that this type of exchange reaction might also occur between tetraalkyltin compounds and fluorophosphoranes was first suggested to us by the above boron system. If successful this reaction would provide a rather useful synthetic route to alkylfluorophosphoranes. Indeed we have shown that this reaction does serve to give good yields, generally about 60%, of monoalkyltetrafluorophosphoranes. We were not successful in using this reaction to prepare di- or trisubstituted fluorophosphoranes, however, though perhaps under other conditions such syntheses by this

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[5] H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963). An attempt to prepare the salt $(CH_3)_3Sn(NH_3)_2^+PF_6^-$ was made using the metathetical reaction between $(CH_3)_3Sn(NH_3)_2^+Cl^-$ and $NH_4^+PF_6^-$ in aqueous solution. Small amounts of tin–oxygen compounds could be removed by washing the solid formed with chloroform. Analyses showed, however, that even with most careful techniques it was not possible to obtain this compound analytically pure. The best analysis: Calcd. for $C_3H_{15}F_6N_2PSn$: C, 10.50; H, 4.39; N, 8.17. Found: C, 9.52; H, 4.43; N, 6.85. It should be noted nevertheless that the infrared spectrum of this substance verified completely the above conclusions arrived at less directly.

[6] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959).

[7] (a) F. E. Brinckman and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6218 (1960); (b) A. B. Burg and J. R. Spielman, *ibid.*, **83**, 2667 (1961).

method might be successful. Neither were we able to prepare phenyltetrafluorophosphorane from tetraphenyltin by this reaction.

Though our first attempts with this reaction indicated that all the phosphorus was not obtained as volatile phosphorus fluorides, we had difficulty in determining the reason for this observation. Phosphorus pentafluoride is rapidly hydrolyzed by traces of water to give hydrogen fluoride which can then react with glass giving silicon tetrafluoride and water to continue the hydrolysis. If such a reaction were to occur, nonvolatile phosphates or fluorophosphates might account for this decrease in volatile phosphorus-containing products of this reaction. However after some initial difficulties we were able to maintain our reaction system sufficiently dry so that no silicon tetrafluoride and only small traces of phosphorus oxytrifluoride were obtained, and we concluded from this that hydrolysis was not the major reason for the lack of volatile phosphorus-containing products.

This absence of approximately 20% of the phosphorus in the volatile components of this system prompted us to investigate the composition of the solid nonvolatile residue always remaining in the reaction bulb after the reaction. The obvious possibility that the phosphorus pentafluoride was either retained physically by the solid or was coordinated to the solid in an acid-base coordination complex was not supported by the failure to obtain phosphorus pentafluoride when the solid residue was slowly heated to 110°. The appearance of an oily liquid and traces of volatile products indicated that decomposition did occur in this process, but the resulting mixtures of products could not be identified.

The first evidence for the presence of a phosphorus-fluorine-containing species was obtained from the infrared spectra of the solid reaction residue. Handling this residue under nitrogen we were able to obtain satisfactory and reproducible Nujol mull spectra, which in addition to indicating the presence of the expected product trimethyltin fluoride showed complex broad absorption maxima around 800 cm.$^{-1}$, the range expected for phosphorus-fluoride stretching frequencies. The complex which produced this absorption was rather moisture sensitive as soon became evident; after the sample had been allowed to stand in air for a short time infrared peaks in the P—O and P=O regions were observed. After standing 2 weeks the phosphorus-fluorine stretching frequencies were no longer observed.

The possibility that the nonvolatile phosphorus-containing species in the residue was $(CH_3)_3SnPF_6$, similar to the compounds $(CH_3)_3SnX$ ($X = BF_4$, ClO_4, AsF_6, SbF_6)[5,8] reported by Clark, *et al.*, and similar to the compound $(CH_3)_3SnPF_6$ suggested but not characterized by these authors[8] seems to us most logical. The structure of such a complex would be expected to consist of planar trimethyltin groups bridged by PF_6 groups in the axial positions of a trigonal bipyramid. From this structure one would predict an infrared spectrum which would show a terminal P-F stretching maximum at about 800 cm.$^{-1}$. The trimethyltin infrared absorptions would be expected to lie rather close to the similar absorptions in $(CH_3)_3SnF$ in which the trimethyltin units are also planar.

In an attempt to obtain further evidence for this complex, chemical degradations with water and ammonia were attempted. The results with water were inconclusive. Hydrolysis yielded a strongly acid solution as might be expected from the reaction

$$(CH_3)_3SnPF_6 + H_2O \longrightarrow (CH_3)_3SnOH + H^+ + PF_6^-$$

However, in acid solution the hexafluorophosphate anion is known to hydrolyze rapidly to hydrofluoric and a series of fluorophosphoric acids. Titration of the quantity of acid present (as a measure of the quantity of solid $(CH_3)_3SnPF_6$ present) was unsatisfactory. So was a gravimetric fluoride determination. Both acid and fluoride values varied over a wide range of values, presumably because of varying degrees of hydrolysis of the PF_6^- anion.

The reaction with ammonia was conceived to allow us to maintain a basic system.[5] Approximately 2 moles of ammonia per g.-atom of phosphorus expected in the residue was observed to be absorbed by the solid, as predicted for the reaction

$$(CH_3)_3SnPF_6 + 2NH_3 \longrightarrow (CH_3)_3Sn(NH_3)_2^+ + PF_6^-$$

Identification of the solid from this ammonia reaction mixture of the above complex and $(CH_3)_3SnF$ was obtained by comparison of the infrared spectrum of this mixture with known spectra. The ammonia complex was soluble in water without decomposition of the PF_6^- anion, giving a nonacid solution, and the presence of the PF_6^- anion was further ascertained by precipitating it with the tetraphenylarsonium cation.

The compound $(CH_3)_3SnPF_6$ most probably arises from a reaction between phosphorus pentafluoride and trimethyltin fluoride, the latter substance being formed in the exchange reaction producing alkyltetrafluorophosphoranes. To test the validity of this hypothesis the direct reaction of these two reagents was attempted. A decrease in the amount of volatile phosphorus compounds was observed, and the solid retained in the bulb appeared identical with the solid in the tetraalkyltin-phosphorus pentafluoride reaction in all properties.[9]

Though methyltetrafluorophosphorane might also be expected to undergo reaction with trimethyltin fluoride such a reaction was not observed to occur, using the conditions in which a reaction was observed with phosphorus pentafluoride. This is most probably due to the lower Lewis acid strength of the alkylfluorophosphoranes.[10]

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(8) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 1020 (1963).

(9) In the reaction of tetramethyltin and boron trifluoride,[7b] formation of $(CH_3)_3SnBF_4$ is observed to occur. It is probable that this substance arises in a similar manner.

(10) E. L. Muetterties and W. Mahler. *Inorg. Chem.*, **4**, 119 (1965).

We are now engaged in further study of analogous systems.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Reactions of Organotin Compounds. V. Studies of Additional Tri- and Diorganotin Derivatives[1]

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In a further study of five-coordination of tin in compounds of the type R_3SnX, triphenyltin perchlorate and nitrate have been studied spectroscopically. It is concluded that their structures are probably identical with those of their methyl analogs. Contrary to previous reports, triphenyltin nitrate was found to be stable under anhydrous conditions. Studies of trimethyltin sulfate and chromate are reported. The infrared spectrum of dimethyltin chromate provides strong evidence for coordination by the chromate group and further emphasizes the remarkably strong interaction that is consistently observed between the R_3Sn^+ and R_2Sn^{2+} ions and all anions.

Introduction

Five-coordination of tin has been proposed for a number of trialkyltin derivatives, including those of very strong acids, *e.g.*, trimethyltin perchlorate,[2] trimethyltin tetrafluoroborate,[3,4] and trimethyltin hexafluoroantimonate.[4] In at least one instance,[5] chloro(trimethyl)pyridinetin(IV), a full X-ray structure determination and infrared spectroscopic studies conclusively establish both the planarity of the trimethyltin group and the five-coordination of tin. For the derivatives of strong acids, much of the evidence has been obtained by infrared spectroscopy whereby "coordination" by, say, perchlorate to trimethyltin has been deduced from the observation that the perchlorate has C_{2v} (or lower) symmetry, in accord with behavior as a bidentate or bridging group. Such a lowering of symmetry in the solid state could be attributed to coordination, a conclusion reached from similar evidence for some transition metal complexes, *e.g.*, $Cu(ClO_4)_2$,[6] and 3,5-lutidine complexes of nickel(II) perchlorate and tetrafluoroborate.[7] Alternatively, crystal field effects (*i.e.*, low site symmetry) could produce such spectroscopic effects, and this possibility will be considered more fully later in this paper. If coordination of X to R_3Sn occurs, three questions are raised: (i) Does the nature of R have any influence on the interaction between R_3Sn and X? (ii) What is the nature of the interaction? (iii) Do similar effects occur between X and R_2Sn in the derivatives R_2SnX_2? In attempting to distinguish between coordination and crystal field effects and to answer these questions we have (a) examined two triphenyltin compounds, since on analogy with the triphenylcarbonium ion the triphenyltin cation may well possess greater stability than trialkyltin cations, (b) attempted the preparation of triorganotin derivatives of some transition metal oxyanions, and (c) studied dimethyltin chromate.

Experimental

Compounds were prepared and handled by conventional vacuum techniques or under a nitrogen atmosphere in a drybox. Solvents were of either Spectro grade or Mallinckrodt A.R. grade. Infrared spectra were determined using a Perkin-Elmer Model 21 double-beam recording spectrophotometer (NaCl optics) and a Perkin-Elmer Model 421 spectrophotometer. Samples were prepared in the drybox as mulls in Nujol, hexachlorobutadiene, or halocarbon oil.

Triphenyltin Perchlorate.—Anhydrous silver perchlorate (1.092 g.) and triphenyltin chloride (2.030 g.) were shaken in anhydrous ether for 3 days. Silver chloride was filtered off, and the solvent was removed under vacuum at room temperature, to leave a white solid. *Anal.* Calcd. for $C_{18}H_{15}SnClO_4$: C, 48.2; H, 3.34. Found: C, 48.9; H, 3.38. Triphenyltin perchlorate is very soluble in both methanol and ether and is hydrolyzed in moist air, becoming liquid after approximately 1 day.

Anhydrous ammonia (dried over sodium metal) was condensed onto a sample of the solid perchlorate, and onto a solution of the perchlorate in anhydrous methanol. Both mixtures were kept at −70° for 24 hr., after which the excess ammonia and solvent were removed *in vacuo*, to leave white solids. Analytical results were not reproducible but were always of the same order, a typical result being as follows. *Anal.* Calcd. for $C_{18}H_{21}SnClO_4N_2$: C, 44.75; H, 4.35; N, 5.79. Calcd. for $C_{18}H_{18}SnClO_4N$: C, 46.35; H, 3.86; N, 3.00. Found: C, 44.63; H, 4.63; N, 3.99. X-Ray powder photographs showed that all mixtures contained ammonium perchlorate.

Triphenyltin Nitrate.—(a) Silver nitrate (1.00 g.) and tri-

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(1) Part IV: *J. Organometal. Chem.*, in press.

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