three fractions: (1) 1.8 g., b.p. 110–118°, *ca.* 10% $(CH_3)_3SiOSi(CH_3)_3$, 45% product, and 45% THF, by gas chromatography; (2) 8.5 g., b.p. 118–122°, essentially pure product[11] (lit.[12] b.p. 116–117°); (3) 2.2 g., b.p. above 122°, *ca.* 50% product and 50% $(CH_3)_3GeOGe(CH_3)_3$; total yield of product, 10.4 g. (67%). This compound also was readily hydrolyzed by atmospheric moisture.

The Reaction of Phenyllithium with $(CH_3)_3SiOGe(CH_3)_3$ and with $(CH_3)_3SiOSn(CH_3)_3$.—An ethereal solution of C_6H_5Li (*ca.* 20 ml. of 0.1 *M* solution) was added to 20 mmoles of the hexamethyldimetaloxane in 50 ml. of THF. Ether and THF were distilled from the mixture until the temperature at the distillation head was 65°. The resulting solution was heated at reflux overnight. Water then was added, the layers were separated, and the aqueous layer was extracted with THF. The combined organic layers were dried over anhydrous $CaSO_4$ and distilled into a single receiver. The more volatile material was collected at atmospheric pressure, while the high boilers were collected at reduced pressure (bath temperature *ca.* 200° at 0.1 mm.). The resulting solutions were analyzed first qualitatively by gas chromatography. Peaks corresponding to the trimethylphenylmetal derivative and the hexamethyldimetaloxane formed were collected and identified by comparison of their infrared spectra with those of authentic samples. Quantitative gas chromatographic analysis of the trimethylphenylmetal compounds was carried out on a Dow Corning 710 silicone fluid-on-Chromosorb P column with jacket temperature 200° and 15 p.s.i. helium carrier gas. Indene was used as internal standard. These results were obtained: **$(CH_3)_3SiOGe(CH_3)_3$.** Only $(CH_3)_3GeC_6H_5$ and $(CH_3)_3SiOSi(CH_3)_3$ were formed; the former compound was formed in 93.3 and 95% yield in the two runs carried out. One mole % of $(CH_3)_3SiC_6H_5$ would have been detected under the conditions of the analysis if this compound had been formed. **$(CH_3)_3SiOSn(CH_3)_3$.** Only $(CH_3)_3SnC_6H_5$ and $(CH_3)_3SiOSi(CH_3)_3$ were detected in the gas chromatographic analysis. In four runs the former compound was formed in yields of 64.2, 66.8, 69.9, and 79.0%. The significant feature of both sets of experiments is the absence of $(CH_3)_3SiC_6H_5$.

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[11] *Anal.* Calcd. for $C_6H_{18}OSiGe$: C, 34.83; H, 8.77. Found: C, 34.44; H, 8.27.

[12] H. Schmidbaur and M. Schmidt, *Chem. Ber.*, **94**, 1138 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

The Reaction of Iodine Monochloride and $HICl_2$ with Hexaphenylcyclotriphosphazene[1]

BY R. D. WHITAKER,[2] J. C. CARLETON,[3] AND H. H. SISLER

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The existence of addition compounds of iodine monochloride and ordinary heterocyclic amines[4] has been established. Since Shaw and co-workers[5] have found that the basicity of fully substituted aminocyclophosphazenes is comparable with that of free amines, it would seem that information about the basicity of cyclophosphazenes could be gained by studying the interaction of iodine monochloride with one of the cyclophosphazenes. It has been assumed by these workers that the ring nitrogen atoms are the basic centers rather than the exocyclic nitrogen atoms.

We decided to study a fully substituted cyclophosphazene which does not contain exocyclic nitrogen atoms so that any Lewis acid–base interaction would more definitely involve the ring nitrogen atoms. Furthermore, a cyclotriphosphazene was used because the ring is planar and thus is somewhat analogous to the ordinary aromatic heterocyclic amines.

We have found that hexaphenylcyclotriphosphazene and iodine monochloride do not react directly in dry carbon tetrachloride to give a solid adduct. The presence of moisture, however, results in the formation of hydrogen chloride by the hydrolysis of iodine monochloride and causes precipitation of a small amount of crystalline solid having the empirical formula $[(C_6H_5)_2PN]_3 \cdot HICl_2$. The addition of hydrogen chloride to the solution of iodine monochloride causes a significant increase in the yield of this crystalline substance. The heterogeneous reaction of the pure phosphazene and pure iodine monochloride carried out in the strict absence of moisture yields $[(C_6H_5)_2PN]_3 \cdot 2ICl$. Structural studies on these two new adducts of hexaphenylcyclotriphosphazene have not been carried out. However, in view of the known basicity of the phosphazene ring established by Shaw and his co-workers,[5] it seems reasonable to formulate $[(C_6H_5)_2PN]_3 \cdot HCl \cdot ICl$ as $([(C_6H_5)_2PN]_3H)^+ICl_2^-$. Since the two compounds have similar superficial characteristics the structure $([(C_6H_5)_2PN]_3I)^+ICl_2^-$ is a reasonable possibility for the compound $[(C_6H_5)_2PN]_3 \cdot 2ICl$.

Bode, Bütow, and Lienau[6] reported the formation of a salt from the reaction of hexachlorocyclotriphosphazene and perchloric acid. Hence we carried out a similar experiment with ICl and also with $HICl_2$ using the triphenyltrichlorocyclotriphosphazene. However, we observed no reaction between 2,4,6-trichloro-2,4,6-triphenylcyclotriphosphazene[7] and ICl or $HICl_2$ in carbon tetrachloride.

Our results can be interpreted in terms of the assumption that the ring nitrogen atoms in the cyclotriphosphazenes are basic centers and that in the absence of strongly electronegative substituents on the phosphorus atoms their basicity is similar to that of ordinary aromatic heterocyclic amines. Furthermore, it appears that the introduction of electronegative substituents on the phosphorus atoms sharply reduces this basicity.

Experimental

Chemicals.—Iodine monochloride (m.p. 26.5°; lit.[8] 27.2°)

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[1] Trimer of diphenylphosphonitrile.

[2] N. S. F. Summer Research Participant.

[3] Participant in N. S. F. Summer Research Institute for Secondary School Students.

[4] R. D. Whitaker, J. R. Ambrose, and C. W. Hickam, *J. Inorg. Nucl. Chem.*, **17**, 254 (1961).

[5] S. K. Ray and R. A. Shaw, *Chem. Ind.* (London), 1173 (1961); D. Feakins, W. A. Last, and R. A. Shaw, *ibid.*, 510 (1962).

[6] H. Bode, K. Bütow, and G. Lienau, *Chem. Ber.*, **81**, 547 (1948).

[7] Private communication from Dr. B. Gruschkin, W. R. Grace and Co., indicates that this compound is probably the *trans* isomer.

was prepared and purified by the method of Booth and Morris.[8] Hexaphenylcyclotriphosphazene (m.p. 228–229°; lit.[9] 228°, 230–232°) was prepared by the reaction of diphenylchlorophosphine and hydrazine monohydrochloride.[9] A sample of 2,4,6-trichloro-2,4,6-triphenylcyclotriphosphazene (m.p. 155–156°) was kindly furnished by W. R. Grace and Company.

$[(C_6H_5)_2PN]_3 \cdot HICl_2$.—Iodine monochloride was added to CCl_4 which had been saturated with HCl. The resulting solution of $HICl_2$ (*ca.* 0.1 *M*) was slowly added with stirring to a saturated solution of $[(C_6H_5)_2PN]_3$ in CCl_4 (*ca.* 0.02 *M*) until precipitation was complete. The yellow powder was collected by suction filtration, washed with pure solvent until the washings were colorless, and dried in a desiccator. The melting point was 197–199° and the yield was 65% based on the phosphazene. The infrared spectrum of this substance proved that the hexaphenylcyclotriphosphazene ring system remained intact.

Anal. Calcd. for $[(C_6H_5)_2PN]_3 \cdot HICl_2$: C, 54.29; H, 3.93; Cl, 8.9; N, 5.28. Found: C, 54.20; H, 3.83; Cl, 8.4; N, 5.21.

$[(C_6H_5)_2PN]_3 \cdot 2ICl$.—An excess of liquid ICl was added to a small amount (*ca.* 0.25 g.) of $[(C_6H_5)_2PN]_3$, the mixture placed in a vacuum desiccator, and the pressure reduced to 0.1–0.2 mm. for a period of 40 hr. During this time, the excess ICl evaporated and the melting point of the product slowly increased. The mixture also changed from a dark red liquid to a yellow powder during the first 10–12 hr. The final melting point was 181–183° (dec.). The infrared spectrum of this substance showed the presence of the hexaphenylcyclotriphosphazene ring system.

Anal. Calcd. for $[(C_6H_5)_2PN]_3 \cdot 2ICl$: C, 46.88; H, 3.28; Cl, 7.7; N, 4.56. Found: C, 45.21; H, 3.38; Cl, 8.8; N, 4.65.

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[8] H. S. Booth and W. C. Morris, *Inorg. Syn.*, **1**, 167 (1939).

[9] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIFORNIA

On the Reaction of Pentafluorosulfur Hypofluorite with Unsymmetrical Two-Carbon Alkenes

BY STANLEY M. WILLIAMSON

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The reaction of pentafluorosulfur hypofluorite with some simple alkenes and some other compounds has been reported recently.[1] It was found in that work that F_5SOF reacts with vinyl chloride to give exclusively 2-chloro-2-fluoroethyl pentafluorosulfur oxide. This specificity for the addition now has been further confirmed by the use of vinyl fluoride and vinylidene fluoride as reactants. The preparation and physical properties of and structural evidence for 2,2-difluoroethyl pentafluorosulfur oxide and 2,2,2-trifluoroethyl pentafluorosulfur oxide are presented. The equations for the reactions and Roman numeral symbols for the new compounds are

$$FCH{=}CH_2 + FOSF_5 \longrightarrow \underset{\textstyle I}{F_2CH\text{–}CH_2\text{–}O\text{–}SF_5} \qquad (1)$$

$$F_2C{=}CH_2 + FOSF_5 \longrightarrow \underset{\textstyle II}{F_3C\text{–}CH_2\text{–}O\text{–}SF_5} \qquad (2)$$

Experimental

Preparation.—The general description of the gas phase reaction is given elsewhere.[1] The molecular weights of the $CFH{=}CH_2$[2] and $CF_2{=}CH_2$[3] indicated high purity. The extreme reactivity of the F_5SOF toward either of the alkenes made it difficult to follow the reaction quantitatively by means of a pressure drop. A careful product analysis was necessary to determine the presence of any side reaction products or the other isomer of the addition compound. By means of ordinary vapor phase chromatography and fractional co-distillation,[4] there was observed to be essentially no carbon-containing fractions except the one which was the addition product.

Physical Properties.—Some of the physical properties of the compounds are listed in Table I.

TABLE I
PHYSICAL PROPERTIES

	$F_2CH\text{–}CH_2\text{–}O\text{–}SF_5$	$F_3C\text{–}CH_2\text{–}O\text{–}SF_5$
Phase description at room temp.	"Water-clear" liquid	"Water-clear" liquid
Boiling point[a]	62.4°	41.7°
ΔH_{vap}, kcal. mole^{-1}	7.86	7.08
Melting point[b]	$-93 \pm 1°$	$-108 \pm 1°$
Infrared frequencies,[c] cm.$^{-1}$	890 (s), 905 (s), 960 (w) 1079 (m), 1103 (m), 1141 (w) 1372 (w), 1420 (w), 1463 (w) 2987 (w)	891 (s), 916 (s) 975 (w), 1100 (m) 1187 (s), 1299 (m) 1415 (w), 2988 (w)
Liquid density, g./ml. at 25.0°	1.680	1.670

[a] The normal boiling points were determined from the vapor pressure *vs.* temperature data. The constancy of the vapor pressure *vs.* temperature from various fractions of the sample was taken as additional evidence of the purity of the compounds. The other evidence seemed to rule out the possibility of having azeotrope formation. [b] The melting points were observed under autogenous pressure. The visual observation was made on the sample as it warmed slowly in a *n*-propyl alcohol cold bath. The compounds have a strong tendency to form glasses when the liquid is cooled. When the compounds were distilled slowly into a cold trap at −183°, the condensing vapor usually would crystallize instead of forming a glass. [c] The infrared spectra were taken on a Perkin-Elmer 421 grating spectrophotometer at 2 mm. gas pressure in a 10-cm. glass cell with NaCl windows. The relative intensities of the absorptions are in parentheses following the frequency.

Structural Evidence.—Chemical analyses and vapor densities confirmed the formation of an addition compound.

Anal. Calcd. for $C_2H_3SOF_7$: C, 11.6; H, 1.5; S, 15.4; F, 64.0. Found: C, 11.9; H, 1.7; S, 15.2; F, 65.0. The theoretical vapor density of $C_2H_3SOF_7$ is 208.1 g./g.m.v. The experimental value was 209.8, which was measured at 142.0 mm. pressure and 299.5°K.

Anal. Calcd. for $C_2H_2SOF_8$: C, 10.6; H, 0.9; S, 14.2; F, 67.3. Found: C, 10.6; H, not determined; S, 14.5; F, 68.4. The theoretical vapor density of $C_2H_2SOF_8$ is 226.1 g./g.m.v. The experimental value was 227.8, which was measured at 238.0 mm. pressure and 298.8°K.

The observed frequencies of infrared absorptions are consistent with those which have been observed before for similarly structured compounds.[1] ($FCH_2\text{–}CH_2\text{–}O\text{–}SF_5$ has infrared absorption frequencies for carbon–fluorine at 1068 and 1098 cm.$^{-1}$, whereas for $CF_3\text{–}CF_2\text{–}O\text{–}SF_5$ they are at 1110, 1196, and 1246 cm.$^{-1}$.) The main pentafluorosulfur oxide frequencies for the compounds reported in this note are well within the range of 888 and 935 cm.$^{-1}$ reported for F_5SOF.[5] It appears now that with the growing number of F_5SO derivatives, the original assignment[5] in F_5SOF of the 888 cm.$^{-1}$ frequency to the O–F stretch was not correct. A more thorough study of these spectra will be required before a definite assignment can be made.

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[1] S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962).

[2] A gift from Dr. J. Nelson, Jackson Laboratory, E. I. du Pont de Nemours Company, Wilmington, Delaware.

[3] Purchased from Peninsular Chemresearch Inc., Gainesville, Florida.

[4] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

[5] F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 1553 (1956).