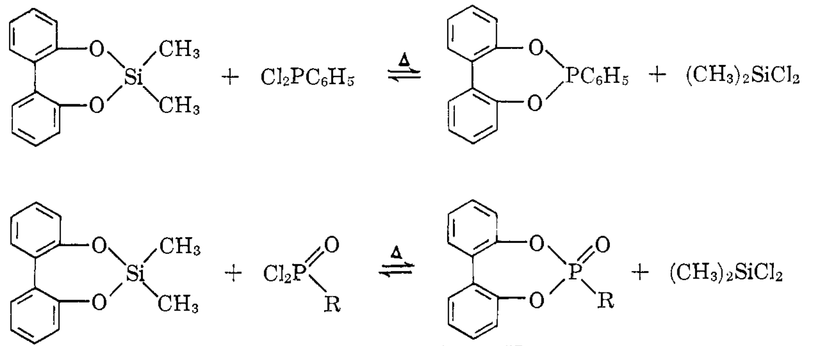
Transformations of Heterocycles. The Conversion of Cyclic Esters of Silicon into Their Phosphorus(III) and Phosphorus(V) Analogs in One Step

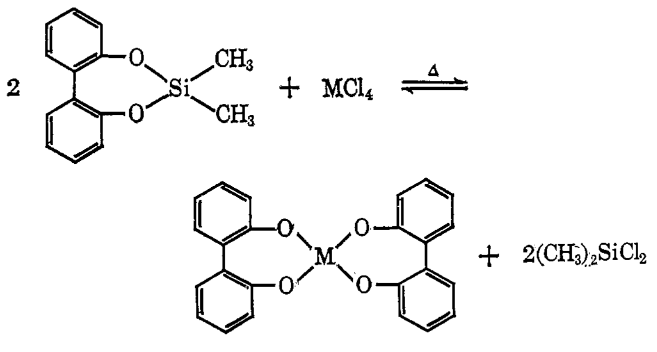
Sir:

We report the transformation of silicon–oxygen heterocyclic systems into their phosphorus(III) and phosphorus(V) analogs through the simple one-step reaction of the silicon compound with the dichlorides of organophosphines and phosphine oxides. Single-ring heterocycles can also be converted into their spiro derivatives by this method. The driving force of the reactions results from the removal of the more volatile product from the refluxing reaction mixture.

Schmutzler has reported reactions in which the Lewis acids phenyltetrafluorophosphorane and diphenyltrifluorophosphorane have cleaved disiloxanes[1] and, similarly, silicon–nitrogen bonds are cleaved by covalent halides of groups III, V, and VI.[2] In our experiments 2,2′-diphenylenedioxydimethylsilane[3] was refluxed with phenyldichlorophosphine, phenyldichlorophosphine oxide, and chloromethylphosphonic dichloride as


R = C_6H_5, CH_2Cl

Reactions with silicon tetrachloride and germanium tetrachloride gave bis(2,2′-diphenylenedioxy)silane[4] and bis(2,2′-diphenylenedioxy)germane.[5]


M = Si, Ge

The mixing of 2,2′-diphenylenedioxydimethylsilane with phenyldichlorophosphine is slightly endothermic. The formation of dimethyldichlorosilane in benzene solutions of the reactants at room temperature can be followed by nmr, where only very small ratios of dimethyldichlorosilane to silicon starting material are found after 24 hr. In the transformations as carried out, the lowest-boiling component, dimethydichlorosilane (bp 70°), was effectively distilled from the system and allowed to hydrolyze on contact with atmospheric moisture at the mouth of a drying tube on top of the reflux condenser.

2,2′-Diphenylenephenylphosphonite. To 0.31 mole of 2,2′-diphenylenedioxydimethylsilane in a nitrogen atmosphere was added 0.31 mole of dichlorophenylphosphine. The temperature was maintained at 150° for 48 hr, with stirring, during which time sticky droplets of hydrolyzing dimethyldichlorosilane dropped from the drying tube on top of the condenser. The product was distilled at 215° (1 mm) and solidified on standing overnight. *Anal.* Calcd for $C_{18}H_{13}O_2P$: C, 74.0; H, 4.45; P, 10.6; mol wt, 292. Found: C, 74.08; H, 4.70; P, 10.22; mol wt, 279.

2,2′-Diphenylenephenylphosphonate. To 0.12 mole of 2,2′-diphenylenedioxydimethylsilane in a nitrogen atmosphere was added 0.12 mole of dichlorophenylphosphine oxide. The reaction mixture was stirred and the temperature maintained at 125–150° for approximately 29 hr. By the time the temperature in the pot had risen to 125°, the sticky droplets of hydrolyzing dimethyldichlorosilane had started to appear in the drying tube. The clear liquid product was collected at 93–95° (2 mm). Overnight it solidified, mp 116–117°. *Anal.* Calcd for $C_{18}H_{13}O_3P$: C, 70.1; H, 4.22. Found: C, 69.85; H, 4.39.

2,2′-Diphenylenechloromethylphosphonate. To 0.18 mole of 2,2′-diphenylenedioxydimethylsilane under a nitrogen atmosphere was added 0.18 mole of chloromethylphosphonic dichloride. The reactants were heated at 115° for 24 hr during which time droplets of hydrolyzing dichloromethylsilane formed in the drying tube. At the end of 24 hr, the solution had become black. A distillation was attempted, but by 40° *in vacuo* the black liquid had evaporated, leaving a white solid. This solid was sublimed *in vacuo* yielding a white solid, mp 161–163°. *Anal.* Calcd for $C_{13}H_{10}O_3PCl$: C, 55.71; H, 3.58; P, 11.1. Found: C, 55.88; H, 4.02; P, 11.05. The monomer requires mol wt 280; found, 269.

Bis(2,2′-diphenylenedioxy)silane. To 0.24 mole of 2,2′-diphenylenedioxydimethylsilane in a nitrogen atmosphere was added 0.12 mole of silicon tetrachloride. The reaction mixture was heated until no further viscous product formed in the drying tube. After excess

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(4) R. Schwarz and W. Kuchen, *Z. Anorg. Allgem. Chem.*, **279**, 84 (1955); J. J. Zuckerman, *J. Chem. Soc.*, 873 (1962).

(5) R. Müller and L. Heinrich, *Chem. Ber.*, **95**, 2276 (1962); J. J. Zuckerman, *J. Chem. Soc.*, 1322 (1963).

starting material had been distilled, the brown solid residue was sublimed *in vacuo* at 240°. The white solid which collected on the cold finger had an infrared spectrum superimposable with that reported[4] and melted at 330–331°.

Bis(2,2′-diphenylenedioxy)germane. To 0.092 mole of 2,2′-diphenylenedioxydimethylsilane was added 0.045 mole of germanium tetrachloride with constant stirring in a nitrogen atmosphere. The tan solid that had formed was sublimed *in vacuo* after excess starting material was distilled. The infrared spectrum of the product which sublimed at 270° *in vacuo* was superimposable with that reported for bis(2,2′-diphenylenedioxy)germane.[5]

Acknowledgment. The investigation was supported by Public Health Service Research Grant CA-07064-02 from the National Cancer Institute.

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Received September 10, 1965

Two New Fluorides of Oxygen, O_5F_2 and O_6F_2[1,2]

Sir:

In our paper describing the preparation of O_4F_2[3] the likely existence of two new oxygen fluorides, *i.e.*, O_5F_2 and O_6F_2, was postulated.

We wish to describe the preparation of these two fluorides, which at present are characterized mainly by their empirical formulas.

Table I

Experimental conditions	Preparation of O_5F_2 Run no. 1	2	3	Preparation of O_6F_2 Run no. 1	2	3	4
Feed rate of the $5O_2 + 2F_2$ and $6O_2 + 2F_2$ gas mixtures, cm³/hr, at NTP	8.5	8	6	22.5	20.3	15.0	15.0
Pressure in the reaction vessel, mm (±0.1)	8	4	6	2	1	1	0.5
Bath temp, °K (±1°)	70	60–70	77	70	60–61	60	60
Electric power, w (±0.2)	5.3	5.3	4.0	4–6	2	2	1.6
Duration of the expt, hr	3.5	3.0	5.0	0.75	1.5	0.83	1.25
Amount of product obtained, mg	45.0	35.1	45.9	17.3	44.9	17.6	28.0
Empirical formula of reaction product	$O_{4.94}F_{2.00}$	$O_{4.96}F_{2.00}$[a] $O_{5.06}F_{2.00}$	$O_{4.90}F_{2.00}$	$O_{6.00\pm0.15}F_{2.00}$	$O_{5.96\pm0.04}F_{2.00}$	$O_{5.88\pm0.30}F_{2.00}$	$O_{5.89\pm0.25}F_{2.00}$

[a] Analyzed by F_2 absorption with Hg!

They were prepared in the same type of electrical-discharge apparatus as described previously,[4,5] only under much milder conditions as suggested above,[3] that is, (a) in a smaller reaction vessel (9 cm high, 3 cm i.d., 1 cm in diameter, copper electrodes 2.5 cm apart), (b) using less power (only ≃6–2 w), (c) more cooling, *i.e.*, down to a bath temperature of 60°K (using a mixture of liquid O_2–N_2 and pumping), and (d) lower gas discharge pressure (*i.e.*, down to 1 and even 0.5 mm). A gas mixture of the composition $5O_2 + 2F_2$ and $6O_2 + 2F_2$, respectively, was admitted to the discharge vessel at such a rate that the pressure in it remained practically constant. All pertinent details of seven preparations are given in Table I.

The method of analysis is simple and unambiguous. On warming, the two new fluorides—like O_4F_2, O_3F_2, and O_2F_2—finally decompose to O_2 and F_2; infrared spectra established the absence of any O_3 or OF_2. Fluorine was quantitatively determined by treating it with dry KI and determining the I_2 liberated iodometrically; O_2 was determined gas volumetrically in a vacuum system by absorption with alkaline pyrogallol. Any unreacted O_2 or F_2 can be pumped off from the reaction product at 60–70°K. The only possible known oxygen compound which could falsify our analysis is *ozone.* However, it can be extracted from our product by condensing liquid O_2 or N_2; amounts of 0.3 mg of O_3 in 0.3 cc of liquid O_2 or N_2 can be detected easily. However, no ozone was formed.

Thus, for example, if 50 mg of O_6F_2 were to contain 0.3 mg of O_3, the accuracy of the empirical formula would be affected to the extent of only $O_{6.00\pm0.05}F_{2.00}$!

SiF_4 was present in our product in amounts of ≃10 wt % and is due to the action of activated fluorine on glass.

The analyses give only the empirical formulas and do not exclude a mixture of lower oxygen fluorides with higher ones, such as O_7F_2 or O_8F_2. However, we consider such a possibility very unlikely (see experiments with $5O_2 + F_2$ mixtures). Since O_3F_2 and O_4F_2 have been characterized by their epr spectra and found to contain the radical $\cdot$OOF,[6,7] *it is likely* that our new

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[1] This paper describes a part of work sponsored by the Office of Naval Research, Contract Nonr 3085(01).

[2] Presented at the 3rd International Fluorine Symposium, Munich, Germany, Aug 31, 1965.

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