column distillation.[7] In each reaction small quantities of SiH_4 and PH_3 were formed along with the desired products. Bis(phosphino)silane and $SiH(PH_2)_3$ were obtained in yields of 30 and 18%, respectively. Bis(phosphino)silane (mol wt (vapor tension): found, 96.2; calcd, 96.06) has a vapor pressure of 9.0 ± 0.5 mm at 0°. Tris(phosphino)silane has a vapor pressure of *ca.* 2 mm at room temperature.

Bis(phosphino)silane and $SiH(PH_2)_3$ were characterized unequivocally on the basis of data obtained from elemental analyses, reactions with HCl, and mass, infrared, and ^1H and ^{31}P nmr spectral analyses.

Elemental analysis of the samples was accomplished by hydrolysis in dilute aqueous NaOH. The calculated ratio of $SiH_x(PH_2)_{4-x}:PH_3:H_2$ (hydrolytic) according to the reaction shown in eq 3 is, for $SiH_2(PH_2)_2$, 1.00:

$$SiH_x(PH_2)_{4-x} + 2H_2O \longrightarrow SiO_2 + (4 - x)PH_3 + xH_2 \qquad (3)$$
$$x = 1 \text{ or } 2$$

2.00:2.00 (found 1.00:1.96:1.98); for $SiH(PH_2)_3$, 1.00: 3.00:1.00 (found 1.00:2.94:0.97). The reactions of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ with excess HCl resulted in the quantitative formation (>94%) of PH_3, SiH_2Cl_2, and $SiHCl_3$, respectively.

The monoisotopic mass spectra of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ contain peaks at (assignments in parentheses) m/e 28–34 (SiH_x^+ and/or PH_x^+), 59–64 ($SiPH_x^+$), and 90–96 ($SiP_2H_x^+$) and 28–34 (SiH_x^+ and/or PH_x^+), 59–63 ($SiPH_x^+$), 90–95 ($SiP_2H_x^+$), and 121–128 ($SiP_3H_x^+$), respectively. Weak peaks from m/e 64–67 assigned to $P_2H_x^+$ ions are also observed in the spectrum of $SiH(PH_2)_3$. The source of these ions has not been determined; however, it appears likely that they arise because of pyrolysis of the sample in the ionization chamber of the spectrometer. The most intense peaks in the spectra of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ occur at m/e 63 and 95, respectively, corresponding in each case to the loss of a neutral PH_2 fragment from the molecular ion.

The gas-phase infrared spectra in the region 4000–400 cm^{-1} exhibit the following absorptions (in cm^{-1}): for $SiH_2(PH_2)_2$, 2310 (s), 2160 (vs), 1066 (m), 930 (s), 823 (vs), 738 (w), 688 (w), 586 (w), and 482 (w); for $SiH(PH_2)_3$, 2308 (vs), 2152 (s), 1062 (m), 810 (s), 786 (m), 755 (w), 697 (w), 567 (m), and 474 (m). The absorptions at 2310 and 2308 cm^{-1} and 2160 and 2152 cm^{-1} can be assigned to the Si–H and P–H stretching modes, respectively. A complete analysis and assignment of the remainder of the absorptions is in progress and will be reported later.

The 60-MHz ^1H nmr spectrum of $SiH_2(PH_2)_2$ is comprised of a low-field resonance (A) at δ −4.32 ppm[8] of area 2.0, which is assigned to the SiH_2 protons, and a high-feld, complex doublet (B) at δ −1.44 ppm of area 4.0, which arises from the PH_2 protons. Resonance A appears as a 1:2:1 triplet (J = 18.4 cps, H–P coupling in HSiP) of 1:4:6:4:1 quintets (J = 4.9 cps, H–H coupling in HSiPH). Resonance B is a doublet (J = 1855 cps, H–P coupling) in which each doublet member is further split in a complex coupling pattern. The coupling exhibited by the PH_2 protons is consistent with that expected for an $X_2AM_2A'X_2'$ spin-coupling system. The ^1H nmr spectrum of $SiH(PH_2)_3$ consists of a low-field resonance (C) at δ −4.80 ppm of area 1.0, which is assigned to the SiH proton, and a high-field complex doublet (D) at δ −1.79 ppm of area 6.0, which arises from the PH_2 protons. Resonance C appears as a 1:3:3:1 quartet (J = 20.8 cps, H–P coupling in HSiP) of 1:6:15:20:15:6:1 heptets (J = 4.9 cps, H–H coupling in HSiPH). Resonance D is a complex doublet (J = 189 cps, distance between the two most intense peaks of the doublet) in which each doublet member is split in a complex coupling pattern. A complete analysis of the complex coupling situation which exists for the PH_2 protons of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ will be reported in detail elsewhere.[9]

The ^{31}P nmr spectra of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ consist of single 1:2:1 triplet resonances (PH coupling) at δ +252 ± 2 and 216 ± 2 ppm, respectively. Because of the second-order spin–spin coupling which exists in these compounds, each member of the triplets shows additional splitting which we have been unable to adequately resolve so far; however, of essential importance is the fact that only one type of phosphorus atom chemical environment is present in each molecule.

Bis(phosphino)silane and $SiH(PH_2)_3$ are surprisingly stable compounds. Neither compound showed detectable decomposition after periods of *ca.* 1 hr at 37° in the probe of the nmr spectrometer. The stability of $SiH_2(PH_2)_2$ is in marked contrast to that reported for the isoelectronic phosphorus hydride, P_3H_5, which decomposes rapidly at temperatures above −23°.[10]

Further studies of the chemistry of these new ternary silicon–phosphorus hydrides is in progress and will be reported later.

Acknowledgment. This work was supported by the National Science Foundation, the Petroleum Research Fund, and the University of Colorado Council on Research and Creative Work.

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[7] The distillation column is a 30-cm long concentric-tube apparatus of a type designed and used in the laboratories of Professor R. Schaeffer and coworkers, Indiana University, Bloomington, Ind.

[8] Proton chemical shift values are reported relative to internal $(CH_3)_4Si$. Phosphorus-31 chemical shifts are given relative to external 85% H_3PO_4.

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Arlan D. Norman
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

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The Reaction of Dioxygen Difluoride and Perfluoropropene. Preparation of 1-Fluoroperoxyperfluoropropane and 2-Fluoroperoxyperfluoropropane

Sir:

Dioxygen difluoride (O_2F_2) is a very reactive, unstable species. At temperatures above −160°, O_2F_2 decomposes to oxygen and fluorine. The chemistry of O_2F_2 can be explained in two manners. If the reaction is run under conditions causing decomposition of O_2F_2, simple fluorination results. Sulfuryl fluoride (F_2SO_2) is formed in this manner by the reaction of O_2F_2 and sulfur dioxide (SO_2).[1] If this reaction is moderated, the OOF group is transferred from O_2F_2 to form peroxysulfuryl difluoride (FSO_2OOF).[1]

Jackson[2] determined the structure of O_2F_2 by micro-

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(1) I. J. Solomon, A. J. Kacmarek, and J. K. Raney, *Inorg. Chem.*, in press.

(2) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

wave spectroscopy and found that the O–O distance is particularly short (1.217 ± 0.003 Å) and that the O–F distance is particularly long (1.575 ± 0.003 Å). Therefore the weakest bond in O_2F_2 is the O–F bond. Also, the OOF radical exists at low temperatures.[3-5] The reactions of O_2F_2 with boron trifluoride[6] (BF_3) and SO_2[1] have recently been explained in terms of the OOF radical.

Therefore under certain conditions the addition of O_2F_2 to perfluorinated olefins should result in new OOF compounds. Holzmann and Cohen[7] studied the reaction of O_2F_2 and tetrafluoroethylene (C_2F_4) and found the reaction to be very vigorous; at −195° flashes were observed. The main products were carbon tetrafluoride (CF_4) and carbonyl fluoride (COF_2); smaller amounts of hexafluoroethane (C_2F_6), silicon tetrafluoride (SiF_4), and trifluoromethyl peroxide (CF_3OOCF_3) were also present. Reactions of this type can be moderated in at least two ways: by using less reactive perfluoroolefins and by using a solvent.

O_2F_2 and perfluoropropene (C_3F_6) reacted smoothly at −183° in chlorotrifluoromethane ($CClF_3$) to give a respectable yield of a fraction containing 2-fluoroperoxyperfluoropropane [$CF_3CF(OOF)CF_3$] and 1-fluoroperoxyperfluoropropane [$CF_3CF_2CF_2OOF$]. In addition to a combined yield of approximately 20% of these new OOF compounds, small amounts (less than 5% combined) of COF_2, C_2F_6, octafluoropropane (C_3F_8), fluoroperoxytrifluoromethane (CF_3OOF), and SiF_4 were formed. The largest portion of the product consisted of a fraction nonvolatile at −80°, thermally unstable at room temperature, and shock sensitive. The F^{19} nmr spectra of this fraction showed a complex mixture of fluoroalkyl groups. No OF or OOF groups were observed, but some unstable oxygenated compound was present, since a sometimes explosive decomposition to fluorocarbonyl compounds occurred during attempts to purify the mixture.

The perfluoropropyl OOF compounds, once separated from the reaction mixture, appeared to be stable and not shock sensitive. The infrared spectrum showed no change after storage of these compounds for 17 hr at room temperature.

The perfluoropropyl OOF isomers were separated from the other products by fractional condensation, but attempts to separate them from each other were unsuccessful. The reaction mixture was stripped of solvent by distillation through traps at −80, −138, and −196°. The −138° condensate was redistilled through −80, −112, and −126° traps. All attempts to further purify the −112° condensate [fraction shown to contain $CF_3CF(OOF)CF_3$ and $CF_3CF_3CF_3OOF$] by gas chromatography were unsuccessful. Therefore the isomers were characterized without being separated.

The infrared spectrum of n-C_3F_7OOF and i-C_3F_7OOF is similar to other compounds containing the n-C_3F_7 and i-C_3F_7 groups. In addition to the perfluoropropyl absorption, a band at 11.1 μ was observed. It has been reported[8] that 1-fluoroxyperfluoropropane [$CF_3CF_2CF_2OF$] and 2-fluoroxyperfluoropropane [$CF_3CF(OF)CF_3$] contain absorptions at 11.25 and 11.3 μ, respectively, and these bands were assigned to the OF group. Therefore, it is likely that the 11.1-μ absorption in n-C_3F_7OOF and i-C_3F_7OOF is due to the OF group in these compounds.

The molecular weight, by vapor density, agreed with the empirical formula C_3F_7OOF (calcd: 220; found: 215, 211, and 217).

A summary of the data obtained from the F^{19} nmr analysis of the C_3F_7OOF isomers is presented in Table I. The −292-ppm resonance absorption line is significant because it is characteristic of fluorine in the OOF position. Thompson[8] reported that the direct fluorination of salts of trifluoroacetic acid (CF_3COOH) produced a number of products including CF_3OOF and CF_3CF_2OOF. The properties of these new OOF compounds were not given, but Thompson[9] observed that the F^{19} nmr chemical shifts for the OOF fluorine were at −291 ppm. The F^{19} chemical shift for the OOF group of the only other reported OOF compound, peroxysulfuryl difluoride[10] (FSO_2OOF), is also at −291 ppm.[11] It is not surprising that the F^{19} chemical shifts for the OOF groups of CF_3OOF, C_2F_5OOF, FSO_2OOF, $CF_3CF(OOF)CF_3$, and $CF_3CF_2CF_2OOF$ are so similar, since the environment of this fluorine atom does not change until the third nearest neighbor. The F^{19} chemical shift of O_2F_2 is the only exception to this rule, but the bonding in O_2F_2 is entirely different from that in the above OOF compounds.

Table I. Data from F^{19} Nmr Analysis of C_3F_7OOF Isomers

Peak no.	Chemical shift,[a] ppm	Rel peak area	Assignment[b]	Chemical shift for corresponding OF compounds, ppm
1	144.2 (d)	1.00	$\mathrm{(CF_3)_2C}\mathit{F}\mathrm{OOF}$	137.4
2	132.8	0.69	$\mathrm{CF_3C}\mathit{F}_2\mathrm{CF_2OOF}$	127.0
3	96.2	0.66	$\mathrm{CF_3CF_2C}\mathit{F}_2\mathrm{OOF}$	93.9
4	85.0 (t)	0.95	$\mathrm{C}\mathit{F}_3\mathrm{CF_2CF_2OOF}$	82.5
5	80.1	5.77	$\mathrm{(C}\mathit{F}_3\mathrm{)_2CFOOF}$	75.6
6	−292[c]	1.32	$\mathrm{C_3F_7OO}\mathit{F}$	

[a] Relative to fluorotrichloromethane ($CFCl_3$); (d) = doublet; (t) = triplet; no splitting was observed for peaks 2, 3, and 5 because of lack of resolution of the 15-mm coil used. [b] The fluorine atom associated with the peak is italicized. [c] This line actually consisted of two unresolved lines; one line is attributed to each isomer.

An actual estimation of the compositions of the isomers and further support for the structure can be obtained from the peak areas. For example, the ratio of peak 1 to peak 5, both from the isopropyl isomer, agrees well with the theoretical ratio, 1:6. The ratio of peaks 2 to 3 to 4 for the n-propyl isomer is very close to the theoretical ratio, 0.67:0.67:1.00. The ratio of all the C–F peaks for both isomers to the OOF peak should be 7; it is 6.86. Comparison of the relative peak area of one isomer with that of the other can be used to compute composition. Any pair of peaks

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can be used for this calculation, but a good average can be obtained by comparing the total peak area for each perfluoropropyl group. Therefore the per cent of the *n*-propyl isomer is

$$\frac{0.69 + 0.66 + 0.95}{0.69 + 0.66 + 0.95 + 1.00 + 5.77} \times 100 = 25\%$$

The product was thus identified as a mixture of approximately 25% $CF_3CF_2CF_2OOF$ and 75% $CF_3CF(OOF)$-CF_3.

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I. J. Solomon, A. J. Kacmarek, J. N. Keith, J. K. Raney
IIT Research Institute
Chicago, Illinois 60616

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The Total Synthesis of Kasugamycin

Sir:

Kasugamycin, found in 1965,[1] is an antibiotic produced by *Streptomyces kasugaensis*, and exhibits a strong preventive effect against rice blast. The structure (I) was established in 1966 by chemical[2] and X-ray crystallographic[3] studies. We now wish to describe the total synthesis of kasugamycin.[4]

6-Methyl-3,4-dihydro-2H-pyran-2-one[5] (II) was treated with nitrosyl chloride in methylene chloride at −60° to give a dimer of 6-chloro-6-methyl-5-nitrosotetrahydropyran-2-one (III) (97%), mp 74–74.5°.[6] The chloronitroso dimer III was easily hydrolyzed with water at room temperature to give 4-oximino-5-oxohexanoic acid (IV) in the theoretical yield. Direct hydrogenation of III with hydrogen over Pd–C afforded only 3,6-dimethylpyrazine-2,5-dipropionic acid.[7] However, the catalytic reduction of IV with hydrogen over Pt afforded stereoselectively DL-*erythro*-4-amino-5-hydroxyhexanoic acid (V) (71%), mp 184–185°.[8] The *erythro* acid V was lactonized by treatment with Ac_2O at room temperature, affording a N-acetylated lactone (VI) (95%), bp 165–168° (0.22 mm). The lactone VI was reduced with $LiAlH_4$ to a hemiacetal[9] (VII) (70%), mp 139–141°, which by treatment with Ac_2O and pyridine at room temperature gave a dihydropyran (VIIIa) (95%), mp 60–62°, and by refluxing with Ac_2O and pyridine at 118–119° gave an N-diacetyl dihydropyran (VIIIb) (70%), bp 110–111° (3.5 mm). The stereochemistry of VIIIb was confirmed to be *trans* as expected from *erythro* isomer V by its nmr spectrum.[10] On the other hand, forosamine[11] obtained from the acid hydrolysate of spiramycin has a D-*erythro* configuration[12] and has been synthesized from the *erythro* acid V in three steps. The reductive dimethylation of V by Bowman's method[13] followed by lactonization with Ac_2O gave IX (95% over-all yield), bp 114–115° (0.5 mm), which on reduction with $LiAlH_4$ gave DL-forosamine (X). This finding not only supports the *trans* relation of the amino and methyl groups, but presents a new and useful method for the synthesis of a deoxyamino sugar from readily available chemicals.

N-Diacetyldihydropyran VIIIb was treated with nitrosyl chloride under similar conditions as in the case of III, affording the expected chloronitroso dimer XI (83%), mp 75–76°. Displacement with lower alcohols such as CH_3OH, EtOH, and *i*-PrOH in the presence of $Hg(CN)_2$ at room temperature afforded the corresponding α-glycosides of nitroso dimer XIIa, XIIb, and XIIc, respectively, in excellent yields. XIIa, mp 135–136°, mol wt 530.5, was reduced with hydrogen over Pt, followed by separation using an acidic ion-exchange resin to give mono-N-acetyl derivative XIIIa (96%), mp 203–204° as hydrochloride, which by hydrolysis with $Ba(OH)_2$ gave DL-methylkasugaminide (XIIIc) (91%), mp 164–165° as dihydrochloride, showing an nmr identical with that of methylkasugaminide.[14] This evidence indicates that the nitroso group is exclusively introduced in the axial configuration at C-2 by the addition of nitrosyl chloride.[15] Therefore, the synthesis of the deoxyamino sugar moiety of kasugamycin has been accomplished by stereoselective reactions.

The chloronitroso dimer XI was treated with excess 1:2,3:4-di-O-isopropylidene-D-inositol[16] in methylene chloride at 0° in the presence of Ag_2CO_3, $AgClO_4$, and Drielite, followed by hydrogenation over Pt in acetic acid and boiling in 50% acetic acid. The reaction product was carefully purified by chromatography using Amberlite CG-50 (ammonium form) and

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