from the National Science Foundation. We thank Dr. S. J. L. Lippard (Columbia University) for sending us a preprint of his paper (ref 8) prior to publication, and Ms. Kim Freeman for skillful experimental assistance.

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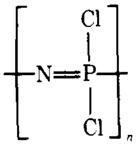
Communications to the Editor

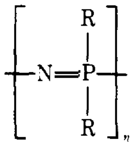
Synthesis of Alkyl and Aryl Phosphazene High Polymers

Sir:

Earlier, we reported the first syntheses of stable, high molecular weight poly(organophosphazenes) of formula $[NP(OR)_2]_n$, $[NP(NHR_2)]_n$, and $[NP(NR_2)_2]_n$[1-3] by the interaction of poly(dichlorophosphazene) (I) with alkoxides, aryl oxides, or amines. Since that time more than 70 different macromolecules based on these structures have been prepared in different laboratories.[4] These species now comprise a new class of high polymers with unusual fundamental and technological properties. However, all these polymers possess organic side groups bonded to phosphorus through oxygen or nitrogen and, for this reason, reaction pathways exist that permit depolymerization or decomposition at temperatures above 200 °C. It was anticipated that a new range of phosphazene polymers, perhaps with higher thermal stabilities and unique physical properties, might be accessible if alkyl or aryl groups could be bonded directly to phosphorus through carbon-phosphorus bonds (II).



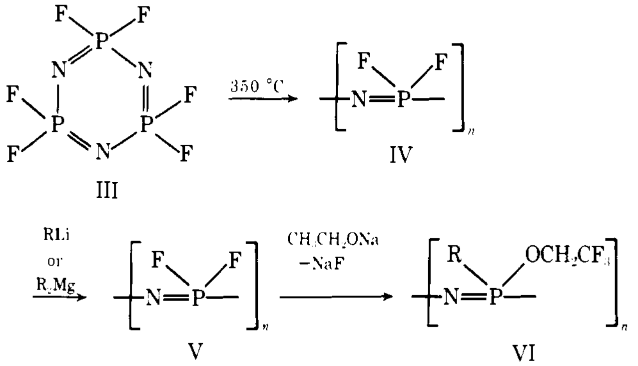
I



II

A few earlier attempts had been made to achieve this end. Polymer I had been allowed to react with Grignard or organolithium reagents,[5,6] but the elemental compositions and properties of these products were incompatible with the expected structures. In fact, earlier work in our laboratory showed that such reagents degrade the phosphazene skeleton of I in preference to replacement of halogen. Similar ring cleavage reactions have been reported when the cyclic $(NPCl_2)_{3\text{ or }4}$ interact with Grignard or organolithium reagents.[7,8] However, small-molecule *fluoro*cyclophosphazenes, such as $(NPF_2)_{3\text{ or }4}$[9,10] are less susceptible to skeletal cleavage under these conditions, and it was of interest to examine the reactions of high polymeric $(NPF_2)_n$ with organometallic reagents.

We report here that high-molecular-weight poly(difluorophosphazene) (IV) is a suitable substrate for reaction with some organometallic reagents. The poly(difluorophosphazene) prepared by the published techniques[11,12] is a cross-linked material that is insoluble in all solvents and cannot be used for substitution reactions. We have found that careful, controlled polymerization of highly purified molten $(NPF_2)_3$ (III) at 350 °C in a high pressure autoclave system for 16-24 h yielded an elastomeric form of IV that was soluble in organic media. Perfluorodecalin on perfluoro-2-butyltetrahydrofuran are suitable solvents, although the addition of 10 vol % of diethyl ether was sometimes necessary to effect complete solution of the polymer. Cross linking and insolubilization of IV normally occur after ~50% of the trimer has been polymerized.



The soluble poly(difluorophosphazene) reacted cleanly with aryllithium reagents or with dialkylmagnesium compounds to yield partly substituted, soluble, high-molecular-weight poly(aryl- or alkylphosphazenes) (V). The remaining fluorine in V was removed by reaction with nucleophiles, such as CF_3CH_2ONa, to yield hydrolytically stable, mixed substituent polymers such as VI. Attempts to achieve total replacement of fluorine in IV led to a marked shortening of the chains, although up to 80-90% of the fluorine could be replaced by alkyl or aryl without the polymer incurring a serious decline in molecular weight. The products of these reactions are flexible or elastomeric materials with unusual combinations of physical properties. The following are examples of typical reactions.

Phenyllithium prepared from bromobenzene (26.2 g, 0.17 mol) and excess lithium in diethyl ether (200 mL) was added to a solution of IV (4.6 g, 0.055 mol) in perfluorobutyltetrahydrofuran (175 mL) and diethyl ether (12 mL) as a heterophase suspension in tetrahydrofuran (THF) (1000 mL). After a 6-min reaction at 21 °C, the mixture was treated with a solution prepared from trifluoroethanol (18 ml, 0.25 mol) and sodium (2.1 g, 0.11 mol) in THF (150 mL). After an 18-h reaction at 61 °C, the polymer was isolated by precipitation in dilute aqueous hydrochloric acid, followed by sequential precipitation from THF into water, acetone, and hexane (yield 41%). The white, flexible, film-forming polymer had a glass transition temperature (T_g) of 60 °C. Infrared and NMR spectra were compatible with structure VI. ^{31}P NMR spectra showed a peak at +2.16 ppm with a shoulder at +7.69 ppm.[13] Gel permeation chromatography (GPC)[14] suggested a molecular weight near 1.2×10^6. Elemental analysis[15] indicated that 62% of the side groups were phenyl and 38% were CF_3CH_2O. Comparative tests indicated that this polymer showed a greater resistance to molecular weight decline at 300 °C than did $[NP(OCH_2CF_3)_2]_n$. Prolonged reaction of IV with phenyllithium (for example, for 12 h at 20 °C) raised the phenyl side group content to 84%,[16] while the molecular weight declined to ≈80 000. More vigorous reaction conditions yielded fully substituted[17] but lower molecular weight materials ($\overline{M}_n \approx 2500$).

Similar techniques were employed for the interaction of diethylmagnesium or dibutylmagnesium in THF or glyme with solutions of IV in perfluorobutyltetrahydrofuran. After a 2-day reaction with Et_2Mg at 25 °C, followed by treatment with CF_3CH_2ONa/CH_3CH_2OH at 60 °C for 24 h, a highly elastomeric polymer was isolated (yield 20%). It was soluble in THF and chloroform. The $\overline{M}_n$ molecular weight by GPC analysis[14] was 6×10^5, and microanalysis indicated that 90% of the side groups were ethyl and 10% were CF_3CH_2O.[18] ^{31}P NMR analysis showed one peak at −15.99 ppm.[13] The T_g value was −50 °C.

It is clear that this synthetic method via polymer IV provides a valuable route to the synthesis of a new class of potentially useful macromolecules.

Acknowledgment. We thank the Office of Naval Research for the support of this work.

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(13) Relative to aqueous 85% H_3PO_4. The ^{31}P spectrum for $[NP(OCH_2CF_3)_2]_n$ shows a peak at +8.2 ppm.
(14) The M_n molecular weights were estimated by gel permeation chromatography comparison with polystyrene standards with the use of 10^6 Styragel columns. The solvent was THF.
(15) Anal. Calcd for $[NP(C_6H_5)_{1.24}(OCH_2CF_3)_{0.76}]_n$: C, 49.88; H, 3.58; N, 6.49; P, 14.35; F, 20.07. Found: C, 50.20; H, 3.55; N, 6.43; P, 14.30; F, 19.60.
(16) Anal. Calcd for $[NP(C_6H_5)_{1.68}F_{0.32}]_n$: C, 67.00; H, 4.65; N, 7.76; P, 17.20; F, 3.37. Found: C, 66.87; H, 4.70; N, 7.67; P, 17.02; F, 3.40.
(17) Anal. Calcd for $[NP(C_6H_5)_2]_n$: C, 72.36; H, 5.85; N, 7.03; P, 15.59. Found: C, 71.27; H, 5.85: N, 6.31; P, 16.33.
(18) Anal. Calcd for $[NP(CH_2CH_3)_{1.60}(OCH_2CF_3)_{0.20}]_n$: C, 41.00; H, 8.03; N, 11.97; P, 26.49; F, 9.74. Found: C, 41.80; H, 7.89; N, 11.79; P, 26.35; F, 9.78.

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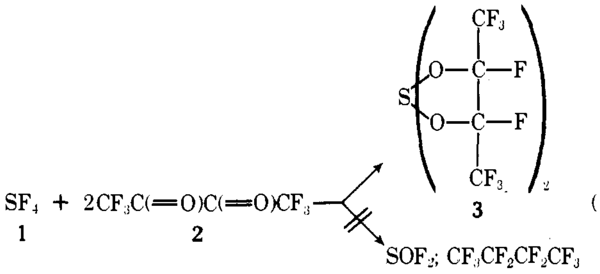
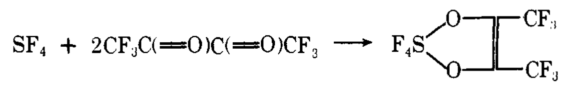
An Unusual Reaction of Sulfur Tetrafluoride with a Carbonyl Compound

Sir:

The reaction of sulfur tetrafluoride with organic compounds containing oxygen functions, such as carbonyl or carboxyl groups, provides a well-established synthesis method of carbon-fluorine compounds.[1] We wish to report a reaction of SF_4 which is in notable contrast to common experience and which takes a highly unexpected course: when SF_4 and perfluorobiacetyl (PFBA) were allowed to react in a 1:2 molar ratio during a period of several days at room temperature, a quantitative yield of a crystalline 1:2 adduct, $SF_4{\cdot}2PFBA$, was obtained, while the expected product, resulting from the fluorination of carbonyl groups, perfluoro-*n*-butane, was not observed (i.e., eq 1). No evidence for the oxidative addition of PFBA to SF_4, with formation of a sulfur(VI)-dioxasulfolene derivative (eq 2), was obtained, either.[2]



(1)

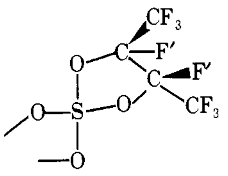


(2)

As will be discussed below our SF_4/PFBA adduct proved to be a spirosulfurane, resulting from transfer of fluorine from sulfur to carbon, with formation of the 1,3,2-dioxasulfolane ring system, as in **3**.[3]

The spirosulfurane **3** was obtained as a white solid of mp 60 °C, stable at room temperature and sufficiently volatile to be sublimed in vacuo (25 °C (1 mm)) without decomposition. The identity of **3** was established by elemental analysis,[4] mass spectroscopy,[5] NMR spectroscopy, and a single-crystal x-ray structure determination.

For the discussion of the NMR data, part of the molecule is drawn as shown in A. The discussion is based on the assumption of a geometry at sulfur approximating to trigonal-bipyramidal, with the two oxygen-containing rings spanning one axial and one equatorial position each, while the lone pair of electrons occupies an equatorial position.[3]



A

In the ^{19}F NMR spectrum of **3** in acetone a second-order multiplet at δ 76.4 ppm[6] is observed for the two nonequivalent CF_3 groups; two signals at δ 122.0 and 129.3 ppm[6] correspond to the nonequivalent fluorine atoms, F′. No change with temperature was observed in the ^{19}F NMR spectrum between 30 and 100 °C (toluene solvent) and between 30 and −70 °C (in acetone). The nonequivalence at room temperature of both CF_3 and F′ substituents is in line with observations on the related sulfurane, $S[OC(CF_3)_2C(CF_3)_2O]_2$.[7] It is believed that the molecule undergoes fast pseudorotation which does not, however, lead to CF_3 and CF fluorine substituents becoming equivalent. Further, our observations suggest trans geometry