the *m/e* 28 peak is nitrogen, of course, and some could be ethyne-d_2 formed by facile isomerization[31,32] of ethenylidene which would arise by loss of nitrogen from **3**.

Work on the kinetics and key intermediates is underway. If the initial steps proposed prove correct, this is further testimony to the lack of reactivity of the diazirine ring.

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References and Notes

(1) S. Braslavsky and J. Heicklen, *Chem. Rev.*, **77**, 473 (1977).
(2) H. Meier and K.-P. Zeller, *Angew. Chem., Int. Ed. Engl.*, **16**, 835 (1977).
(3) J. B. Moffat, "The Chemistry of Diazonium and Diazo Groups," Part I, S. Patai, Ed., Wiley-Interscience, New York, 1978.
(4) E. Schmitz, *Int. Conf. Pure Appl. Chem., 23rd, 1971*, **II**, 283 (1971).
(5) M. Jones, Jr., and R. A. Moss, "Carbenes", Vol. I, Wiley-Interscience, New York, 1973.
(6) M. T. H. Liu and B. M. Jennings, *Can. J. Chem.*, **55**, 3596 (1977).
(7) B. M. Jennings and M. T. H. Liu, *J. Am. Chem. Soc.*, **98**, 6416 (1976).
(8) M. T. H. Liu and K. Toriyama, *Can. J. Chem.*, **51**, 2393 (1973).
(9) H. M. Frey, *Adv. Photochem.*, **4**, 225 (1966).
(10) H. M. Frey and D. E. Penny, *J. Chem. Soc., Faraday Trans. 1*, 2010 (1977).
(11) J. M. Figuera, J. M. Perez, and A. Tobar, *J. Chem. Soc., Faraday Trans. 1*, 809 (1978).
(12) N. P. Smith and I. D. R. Stevens, *J. Chem. Soc., Perkin Trans. 2*, 213 (1979).
(13) R. A. Moss and R. C. Munjal, *J. Chem Soc., Chem. Commum.*, 775 (1978).
(14) Y. Maeda and K. U. Ingold, *J. Am. Chem. Soc.*, **101**, 837 (1979).
(15) E. Schmitz, *Angew. Chem., Int. Ed. Engl.*, **3**, 333 (1964).
(16) A. Lau, *Spectrochim. Acta*, **20**, 97 (1964).
(17) G. F. Bradley, W. B. L. Evans, and I. D. R. Stevens, *J. Chem. Soc., Perkin Trans. 2*, 1214 (1977).
(18) W. H. Graham, *J. Am. Chem. Soc.*, **87**, 4306 (1965).
(19) M. T. H. Liu, manuscript in preparation. All spectral data of the diazirine and its amidine precursor show complete deuteration.
(20) W. E. Jones, C. D. Burkholder, M. Ieki, K. Ling, L. Ramaley, and S. Veysey, *Chem. Biomed. Environ. Instr.*, in press.
(21) J. W. S. Jamieson, G. R. Brown, and J. S. Tanner, *Can. J. Chem.*, **48**, 3619 (1970).
(22) R. A. Witter and P. Neta, *J. Org. Chem.*, **38**, 484 (1973).
(23) L. R. Martin, A. G. Wren, and M. Wun, *Int. J. Chem. Kinet.*, **11**, 543 (1979).
(24) W. E. Jones, S. D. Macknight, and L. Teng, *Chem Rev.*, **73**, 407 (1973).
(25) H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, **55**, 1363 (1933).
(26) P. M. Scott and K. R. Jennings, *J. Phys. Chem.*, **73**, 1513 (1969).
(27) D. T. Clark and J. M. Tedder, *Trans. Faraday Soc.*, **62**, 393, 399, 405 (1969).
(28) P. N. Clough, J. C. Polanyi, and R. T. Taguchi, *Can. J. Chem.*, **48**, 2919 (1970).
(29) W. E. Jones, G. Matinopoulos, J. S. Wasson, and M. T. H. Liu, *J. Chem. Soc., Faraday Trans. 2*, **74**, 831 (1978).
(30) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).
(31) C. E. Dykstra and H. F. Schaefer III, *J. Am. Chem. Soc.*, **100**, 1378 (1978).
(32) J. C. Gilbert, U. Weerasooriya, and D. Giamalva, *Tetrahedron Lett.*, 4619 (1979).

C. D. Burkholder, W. E. Jones,* J. S. Wasson
Department of Chemistry, Dalhousie University
Halifax, Nova Scotia, B3H 4J3, Canada

M. T. H. Liu*
Department of Chemistry
University of Prince Edward Island
Charlottetown, P.E.I., C1A 4P3, Canada

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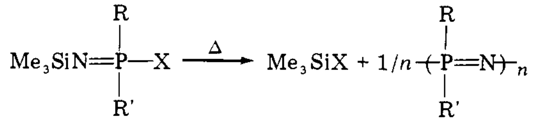
Poly(dimethylphosphazene), $(Me_2PN)_n$

Sir:

The synthesis of fully alkyl- or aryl-substituted polyphosphazenes $(R_2PN)_n$ is a prime objective in phosphazene chemistry because of their anticipated high thermal stability. We report here a new, direct method for the preparation of phosphazenes including the first fully alkylated polyphosphazene, $(Me_2PN)_n$.

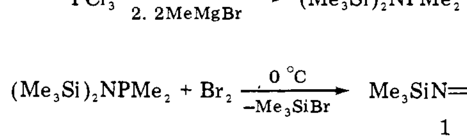
Currently, high molecular weight poly(organophosphazenes) of general formula $[(RO)_2PN]_n$, $[(RHN)_2PN]_n$, and $[(R_2N)_2PN]_n$ are prepared by the nucleophilic replacement of halogen in poly(dihalophosphazene) as developed by Allcock and co-workers.[1] This approach, however, is not generally applicable to the preparation of polymeric phosphazenes containing alkyl or aryl groups linked directly to phosphorus through P-C bonds. Reactions of Grignard and other organometallic reagents with $(Cl_2PN)_n$[2] or $(F_2PN)_n$[3] yield only partially substituted high polymers. If forcing conditions and excess organometallic reagent are employed, significant degradation of the P-N backbone occurs.

Alternatively, our approach is based on the thermal decomposition (eq 1) of suitably constructed *N*-silylphosphinimines. For example, a straightforward sequence of reactions (eq 2-4)[4,5] provides the phosphinimines **1** and **2**, both of which are precursors to the dimethylphosphazenes $(Me_2PN)_n$. Details of the synthesis and characterization of **1** and **2** are reported elsewhere.[5]



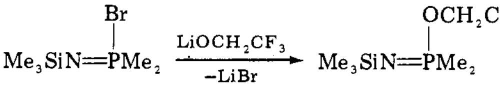
$$\mathrm{Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}X \xrightarrow{\Delta} Me_3SiX + 1/n\,\text{+}\!\!\overset{R}{\underset{R'}{P}}{=}N\!\!\text{+}_n} \quad (1)$$

$$\mathrm{PCl_3 \xrightarrow[2.\ 2MeMgBr]{1.\ (Me_3Si)_2NLi} (Me_3Si)_2NPMe_2} \quad (2)$$



$$\mathrm{(Me_3Si)_2NPMe_2 + Br_2 \xrightarrow[-Me_3SiBr]{0\ ^\circ C} Me_3SiN{=}\overset{Br}{P}Me_2} \quad (3)$$

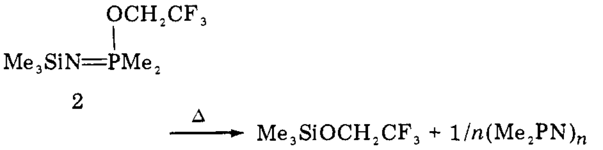
1



$$\mathrm{Me_3SiN{=}\overset{Br}{P}Me_2 \xrightarrow[-LiBr]{LiOCH_2CF_3} Me_3SiN{=}\overset{OCH_2CF_3}{P}Me_2} \quad (4)$$

2

When a neat sample (6.74 g, 27.3 mmol) of the *P*-(trifluoroethoxy)phosphinimine **2** was heated in vacuo in a heavy-walled glass ampoule (~15 mL) for 40 h at 190 °C, decomposition proceeded quantitatively according to eq 5. After the ampoule was opened, $Me_3SiOCH_2CF_3$ (identified by ^1H NMR) was removed in vacuo leaving a gummy white solid which was dissolved in CH_2Cl_2 and removed from the ampoule. Solvent evaporation gave $(Me_2PN)_n$ as an opaque, flexible, polymeric film (2.02 g, 100% yield). The polymer is soluble in CH_2Cl_2, $CHCl_3$, and ethanol, but insoluble in H_2O, acetone, THF, and hexane, A floculent, white, power-like form of the compound (mp 148-149 °C) precipitates when a CH_2Cl_2 solution of the film is poured into hexane. By light scattering, the $\overline{M}_w$ molecular weight is 50 000 corresponding to roughly 650 repeating units. The glass transition temperature of the polymer is −40 °C. By comparison, the polymers of formula $[(RO)_2PN]_n$ and $[(RHN)_2PN]_n$ generally have an average of ~10 000 repeating units. Hence, the glass transition and melting temperatures quoted for $(Me_2PN)_n$ may not represent the limiting values and further efforts are in progress to raise the chain length into the high polymer region. Elemental analysis[6] and IR and NMR spectra are consistent with the formula $(Me_2PN)_n$: ^1H NMR ($CDCl_3$) δ 1.43 (d, J_{PH} = 12.5 Hz); ^{13}C NMR ($CDCl_3$) δ 22.46 (d, J_{PC} = 90.23 Hz); ^{31}P NMR ($CDCl_3$) δ 8.26; IR (thin film) 1300 (s), 1275 (s), 1200 (br, vs) cm^{-1} (P=N). The NMR signals are all sharp lines and there is no indication of the presence of any small ring compounds such as $(Me_2PN)_{3,4}$.



$$\mathrm{Me_3SiN{=}\overset{OCH_2CF_3}{P}Me_2 \xrightarrow{\Delta} Me_3SiOCH_2CF_3 + 1/n(Me_2PN)_n} \quad (5)$$

2

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Prepared in this manner, poly(dimethylphosphazene) bears a superficial resemblance to some lower molecular weight (3500-12 500) products reported by Sisler et al.[7] Their compounds were not characterized by NMR and were obtained only in low yields after a tedious purification process from the thermolysis of $Me_2P(NH_2)_2Cl$. By contrast, our method affords excellent yields and utilizes a conveniently prepared starting material.

The elimination of $Me_3SiOCH_2CF_3$ from *N*-silylphosphinimines is not unprecedented. Flindt and Rose[8] have reported that the symmetrically substituted phosphinimine $Me_3SiN{=}P(OCH_2CF_3)_3$ decomposes at 200 °C to form $[(CF_3CH_2O)_2PN]_n$ of relatively low molecular weight ($\overline{M}_n$ ~10 000).

Interestingly, when the *P*-bromophosphinimine **1** was heated under the same conditions as described for **2**, the product was not a polymer. Instead, a nearly quantitative yield of the cyclic tetramer $(Me_2PN)_4$ was obtained. This marked difference in reactivity probably has important mechanistic implications and, certainly, this aspect of the polymer formation process merits further investigation. As our results demonstrate, however, the elimination of silanes from *N*-silylphosphinimines is an important alternate synthesis of polyphosphazenes, especially those containing P-C-bonded substituents.

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References and Notes

(1) Allcock, H. R. *Angew, Chem., Int. Ed. Engl.* **1977**, *16*, 147.
(2) Allcock, H. R.; Chu, C. T.-W. *Macromolecules* **1979**, *12*, 551.
(3) Allcock, H. R.; Patterson, D. B.; Evans, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6095.
(4) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 347.
(5) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.*, in press.
(6) Anal. Calcd for C_2H_6PN: C, 32.01; H, 8.06; N, 18.66. Found: C, 31.75; H, 8.21; N, 18.32.
(7) Sisler, H. H.; Frazier, S. E.; Rice, R. G.; Sanchez, M. G. *Inorg. Chem.* **1966**, *5*, 327.
(8) Flindt, E.-P.; Rose, H. *Z. Anorg. Allg. Chem.* **1977**, *428*, 204.

Patty Wisian-Neilson, Robert H. Neilson*
Department of Chemistry, Texas Christian University
Fort Worth, Texas 76129
Received December 3, 1979

Preparation, Disproportionation, and Reactions of Two Semi-Met Forms of Hemerythrin

Sir:

The respiratory protein hemerythrin occurs in the erythrocytes of certain marine worms as an octamer of mol wt 107 000. Each subunit contains two linked nonheme irons but there is still a question whether amino acids or oxy bridging is involved.[1-4] The deoxy form has both irons in the oxidation state +2. It is easily oxidized to the met form containing irons only in the +3 oxidation state. We have recently prepared a half-reduced form, in which one of the binuclear irons is +3 and the other +2, by one-electron reduction of methemerythrin with dithionite.[5] An identical species which we designate $(\text{semi-met})_R$ can also be prepared by light irradiation of the met for a short period (1-2 min) in the presence of EDTA and catalytic amounts of a flavin, a method which has been generally effective for the reduction of a number of proteins.[6] Longer irradiation (30 min) leads to near-quantitative production of the deoxy form. We report here some interesting properties of $(\text{semi-met})_R$ and of another form, $(\text{semi-met})_O$, reached from the other direction, namely by one-electron oxidation of the deoxy form by $Fe(CN)_6^{3-}$. The two semi-met forms have quite distinct spectra (Figure 1). Both slowly change to an identical spectrum [allowing for $Fe(CN)_6^{4-}$ present with $(\text{semi-met})_O$] which is close to that of a mixture of equal amounts of met- and deoxyhemerythrin (Figure 1). This is the result of a remarkable spontaneous *first-order* disproportionation (≥85% complete) which occurs within the octamer and leads to four $[Fe^{II}Fe^{II}]$ and four $[Fe^{III}Fe^{III}]$ units in each octamer (Table I). This mixed species behaves like a equimolar mixture of met and deoxy spectrally and kinetically toward O_2 and SCN^-. The disproportionation controls the rate of reaction of the semi-met forms with a number of reagents (see below). Both forms have an EPR spectrum (at liquid He temperatures) with *g* values of 1.95 and 1.71 $(\text{semi-met})_O$ and 1.93, 1.86 and 1.68 $(\text{semi-met})_R$.[7] The disproportionation in solution is accompanied by a decrease in the amplitude of the EPR signal, with an approximate $t_{1/2}$ = 8 min for $(\text{semi-met})_R$[7] at room temperature, consistent with the disproportionation rate constant measured spectrally (Table I). After both semi-met forms have been left for 30 min no EPR signal remains. This would be expected since the met and deoxy forms are EPR inactive,[8,9] even at liquid He temperature.[7] Both semi-met forms react with N_3^- ion to give a single semi-met-azide adduct, with the same electronic and EPR spectrum (g = 1.91, 1.83). This semi-met azide complex is stable toward disproportionation, as shown by a constant spectrum and EPR

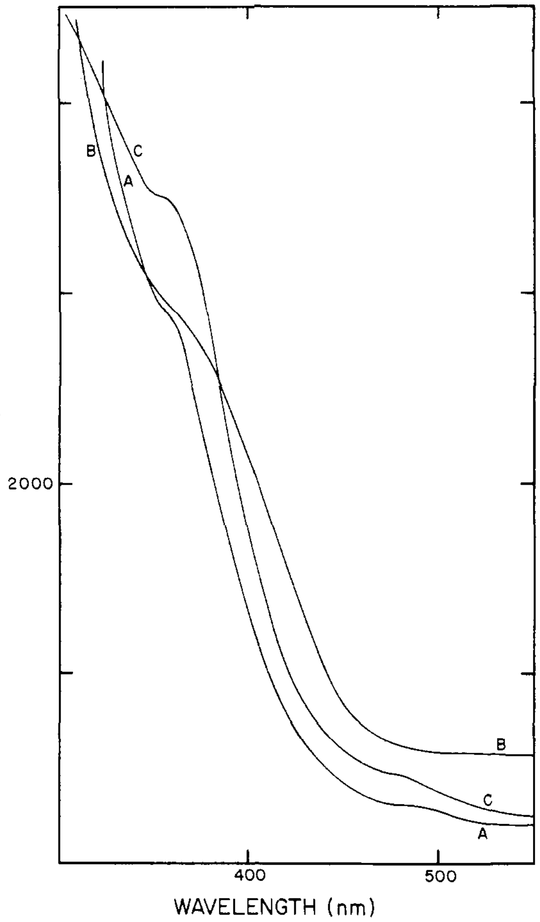

Figure 1. Spectra of $(\text{semi-met})_R$ (A), $(\text{semi-met})_O$ (B), and a common spectrum (C) of disproportionated products from $(\text{semi-met})_O$ and $(\text{semi-met})_R$, as well as an equimolar mixture of deoxyhemerythrin and methemerythrin. $(\text{Semi-met})_R$ was prepared by either addition of 1.3 equiv of $S_2O_4^{2-}$ (per Fe-Fe unit) to met, or by irradiation of methemerythrin (0.1 mM), riboflavin (3-5 μM), and EDTA (5 mM) for 90 s by light from a 300-W projector lamp, 20 cm from the solution. $(\text{Semi-met})_O$ was prepared by addition of 1 equiv of $Fe(CN)_6^{3-}$ to deoxyhemerythrin. Experiments were carried out at pH 8.2, I = 0.15 M and 10 °C.

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