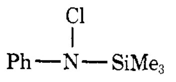
chlorosilane, reaction did take place. The products of that reaction are shown in eq 3. It is significant to note that no azobenzene or trimethylbutylsilane (**11**) was found in either the reaction in which $\mathrm{Me_3SiCl}$ was added to the $\mathrm{PhNHCl{-}PhNH_2}$ mixture or the one in which the $\mathrm{Me_3SiCl}$ was present *in situ* during the addition of the BuLi to the $\mathrm{PhNHCl{-}PhNH_2}$ mixture.

$$\mathrm{PhNHCl + PhNH_2 \xrightarrow[\mathrm{Me_3SiCl}\\ \mathrm{THF,\ -100°}]{\mathrm{BuLi}} PhNH_2\ +}$$

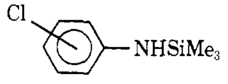
$$\underset{\mathbf{9}}{\mathrm{PhNHSiMe_3}} + \underset{\mathbf{10}}{\mathrm{PhN(SiMe_3)_2}} \text{ and no } \mathbf{8},\ \underset{\mathbf{11}}{\mathrm{BuSiMe_3}},\text{ or BuCl} \qquad (3)$$

We have shown previously that the reaction of BuLi with $\mathrm{Me_3SiCl}$ at $-100°$ occurs in the absence of acidic protons but is slow *relative* to proton abstraction from such things as methylene chloride or chloromethylsilanes.[10] Thus, the absence of **11** in the products of this reaction (eq 3) means that the BuLi preferentially reacted rapidly with PhNHCl (and $\mathrm{PhNH_2}$) rather than combining with $\mathrm{Me_3SiCl}$. When BuLi reacts with PhNHCl, it must remove a proton rather than abstracting a chlorine since no butyl chloride or *N*-butylaniline (**2**), which could come from BuCl and PhNHLi, is found in the products. Since no azobenzene was produced in 2 hr contact of BuLi with PhNHCl (and $\mathrm{PhNH_2}$) at $-100°$, it follows that phenylnitrenoid (**6**) must have existed under those conditions.

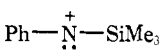
The product of the silation trapping experiment was expected to be, initially, *N*-chloro-*N*-(trimethylsilyl)aniline (**12**). Upon warming, compound **12** was expected to rearrange, *via* the nitrenium ion **15**, to the ring-chlorinated products **13** and **14**. These latter two compounds were prepared by silation of *o*- and *p*-chloroaniline (*via* their lithium derivatives) and shown not to be present in the products of eq 3. It is possible, however, that the nitrenium ion intermediate was formed but that it reacted by way of hydrogen abstraction to afford the observed product **9**.



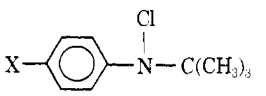
12



13, *o*-Cl
14, *p*-Cl



15a, singlet state
b, triplet state



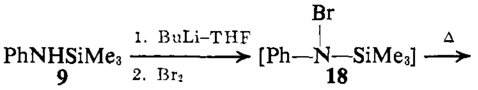
16

Gassman[5] has reported that decomposition of substituted *N*-chloroanilines (**16**) proceeds through nitrenium ions to give both ring-chlorinated and nonchlorinated anilines; in some cases the latter predominate. It is conceivable that the nitrenium ion **15** derived from **12** is very reactive, similar to some of Gassman's compounds, and decomposed by hydride abstraction from the solvent to afford **9** rather than rearranging to **13** and **14**.[11] Alternatively, the neighboring silicon may promote singlet to triplet interconversion of the nitrenium ion (**15a** → **15b**), which then undergoes hydrogen atom abstraction to give **9**. Gassman has shown that halogenated solvents promote singlet–triplet inversions in nitrenium ions and lead to large amounts of hydrogen atom abstraction.[12]

Several experiments have been attempted in order to determine how the nitrenium ion **15** might react in THF. One such attempt is shown in eq 4. The N–Si

$$\underset{\mathbf{17}}{\mathrm{PhNDSiMe_3}} + \mathrm{Ca(ClO)_2} \xrightarrow{?} \mathbf{12} \xrightarrow{?} \mathbf{15} \xrightarrow{?} \mathbf{9} \qquad (4)$$

bond of *N*-trimethylsilylaniline-*N*-d_1 (**17**) is apparently easily cleaved by calcium hypochlorite, since the products of the reaction between these two reagents were aniline and hexamethyldisiloxane ($\mathrm{Me_3SiOSiMe_3}$). Similar results were obtained with the protonated analog of **17**, both with THF and carbon tetrachloride as the solvent. In another attempt, *N*-bromo-*N*-trimethylsilylaniline (**18**) was generated as described in eq 5. The disappearance of the intense bromine color provided evidence that reaction had occurred; yet, as in the case of the chloro analog, no ring-halogenated products (or butyl bromide) were observed; only **9** and some aniline were found.



$$\underset{\mathbf{9}}{\mathrm{PhNHSiMe_3}} \xrightarrow[\text{2. Br}_2]{\text{1. BuLi–THF}} \underset{\mathbf{18}}{[\mathrm{Ph{-}\overset{Br}{\overset{|}{N}}{-}SiMe_3}]} \xrightarrow{\Delta}$$

$$\underset{\mathbf{9}}{\mathrm{PhNHSiMe_3}} + \mathrm{PhNH_2} \qquad (5)$$

In summary, the silation results confirm that phenylnitrenoid **6** is a stable entity at $-100°$ and can serve as a precursor of phenylnitrene. The principal product of the silation reaction, namely **9**, can be accounted for on the hypothesis of a nitrenium ion intermediate **15** reacting primarily by way of hydrogen abstraction from the solvent.

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(10) D. R. Dimmel, C. A. Wilkie, and F. Ramon, *J. Org. Chem.*, 37, 2662 (1972).

(11) Compound 10 probably arises by reaction of 9 with BuLi and, subsequently, $\mathrm{Me_3SiCl}$.

(12) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 5176 (1969).

Charles A. Wilkie,* Donald R. Dimmel*
Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233
Received June 22, 1972

Fluorination of Tetrasulfur Tetranitride and Hexamethylethane. An Indication of the Future of Direct Fluorination

Sir:

The recent development of a technique to control reactions of elemental fluorine with both inorganic and organic compounds has created a potential for synthesis of a large number of new compounds.[1] To illustrate the capabilities of this process in inorganic and organic synthesis, two very difficult problems, one inorganic and one organic, have been chosen for study.

Tetrasulfur tetranitride, $\mathrm{S_4N_4}$, a delicate inorganic ring system, is shock sensitive to a degree that detonations of the pure compound have been observed.[2] Using more conventional techniques, the products of the reaction with fluorine are NSF, $\mathrm{NSF_3}$, and $\mathrm{F_5SN{=}}$

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(1) R. J. Lagow and J. L. Margrave, "The Reaction of Polynuclear Hydrocarbons with Elemental Fluorine," in press; R. J. Lagow and J. L. Margrave, *Chem. Eng. News*, **48**, 40 (Jan 12, 1970).

(2) M. Villena-Blanco and W. L. Jolly, *Inorg. Syn.*, **9**, 98 (1967).

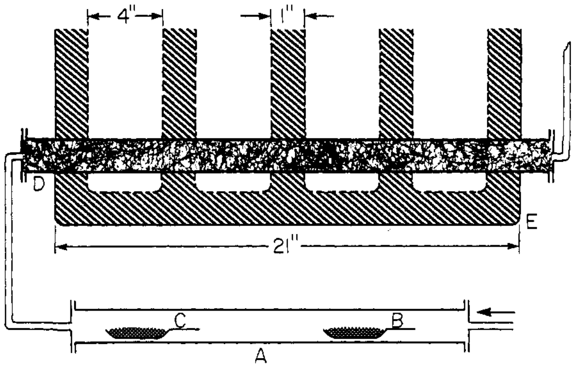

Figure 1. Fluorination reactor.

SF_2,[3] and it has been reported that S_4N_4 reacts violently on contact with a fluorine–nitrogen mixture.[4]

Hexamethylethane was chosen as a reactant because perfluorohexamethylethane, $(CF_3)_3C_2(CF_3)_3$, has not been previously prepared and it has been established that highly branched hydrocarbons are among the most difficult types of compounds to fluorinate.[5,6]

S_4N_4 was prepared according to the synthesis of Jolly.[7] The fluorination apparatus has been previously described in detail.[1] Glass traps equipped with two stopcocks were used to trap volatile products and also as reactors in variable-temperature reactions. In a typical experiment, 0.5923 g (3.32 mmol) of S_4N_4 was finely ground and placed in a nickel boat which was placed in the nickel reactor at room temperature. It was observed that the temperature was a critical parameter in this reaction. The glass trap was attached to the end of the reactor. The system was flushed with helium and the glass trap was cooled to $-78°$ with an 2-propanol–Dry Ice slush. The helium flow was set at 48 cm^3/min and the fluorine at 0.5 cm^3/min. At the end of 8 hr, the fluorine flow was terminated and the system flushed with helium. White crystals of $S_3N_3F_3$, which were unstable to air and glass, were scraped from the walls of the trap inside a drybox (0.507 g, 2.60 mmol). The yield of $S_3N_3F_3$ averaged 81% based on S_4N_4. *Anal.* Calcd for $S_3N_3F_3$: S, 49.28; F, 29.20. Found: S, 48.83; F, 30.04. The infrared bands observed for $S_3N_3F_3$ at 1085, 720, and 650 cm^{-1} (Nujol mull) are in agreement with the previously reported spectrum.[8] The mass spectrum of the material contained a parent peak at 195 and P + 2 peak at 197 due to the ^{34}S isotope. The ^{19}F nmr was run in dioxane and a singlet, which was only slightly concentration dependent ($\sim$2 ppm), was observed at -163 ppm from an external saturated aqueous KF reference. It was also observed that if the residue in the nickel boat was extracted with dioxane, the less volatile $S_4N_4F_4$ was obtained in variable yields as high as 12%. This material was characterized by a parent peak in the mass spectrum at 260 and a singlet in the ^{19}F nmr. The recovery of $S_4N_4F_4$ from the nickel boat and the fact that no $S_4N_4F_4$ was found in the trap would support the hypothesis that $S_4N_4F_4$ is an intermediate in the synthesis of $S_3N_3F_3$.

Hexamethylethane is a solid which is very volatile at room temperature. A new cryogenic reactor (Figure 1) recently developed in our laboratory facilitates the fluorination of room-temperature liquids and gases and increases the sensitivity of the fluorination technique. The nickel reactor A is 18 in. long and 1.5 in. wide. Nickel boat **B** is filled with hexamethylethane and nickel boat C with anhydrous NaF. Reactor A and reactor D are connected by 0.25 in. copper tubing. Reactor D is 24 in. long and 1.5 in. wide and is tightly packed with fluorinated copper turnings. Cold box E is made of stainless steel with an overall depth of 9 in. and width of 6 in. The individual compartments are 4 × 4 × 8 in. and insulated with urethane foam. A glass trap equipped with two stopcocks was attached to the end of the cold reactor. The separated compartments in the cold reactor, aside from their use as a heat sink, were used to create a temperature gradient along the reaction tube and to move the reactants down the tube by successively cooling and warming the various compartments.

In a typical experiment, 0.4237 g (3.71 mmol) of hexamethylethane was placed in a nickel boat. The first two chambers of the cold reactor were filled with Dry Ice–2-propanol slush ($-78°$). The glass trap at the end of the cold reactor was filled with approximately 1 g of NaF and cooled to $-78°$. After flushing the system with helium, the flow was set at 20 cm^3/min and a fluorine flow of 1.5 cm^3/min was initiated. Fifteen hours later, the third compartment of the cold trap was cooled and the first compartment allowed to warm to room temperature. Nine hours later, the helium flow was reduced to 8 cm^3/min. After another 24 hr, the last compartment of the cold reactor was cooled and the second compartment allowed to warm to room temperature. The helium flow was also terminated at this time. Pure fluorine was allowed to run through the system for 32 hr. The fluorine flow was then terminated and a helium flow of 20 cm^3/min started. The last two compartments of the cold reactor were warmed to room temperature. The trap was removed, immersed in liquid nitrogen, and evacuated on a vacuum line. The trap was then warmed to room temperature, allowed to stand for 12 hr, and shaken periodically to allow the HF produced in the reaction to be absorbed by the NaF. The trap was reconnected to the vacuum line and the volatile products were trapped with liquid nitrogen. Mixed fluorocarbons (0.6461 g) were obtained. This mixture was dissolved in CCl_4 and separated on a gas chromatograph at 20°. A 10 ft long, 0.25 in. wide column of 10% SE-30 on Chromosorb P was used. A colorless, volatile crystalline material (0.1525 g, 0.34 mmol) which sublimed at 108° was isolated. A 9.3% yield was obtained based on the initial hexamethylethane. *Anal.* C, 21.93; F, 78.06. Found: C, 21.94; F, 77.72. The ^{19}F nmr consisted of a very strong singlet at -22.0 ppm from an external trifluoroacetic acid reference. The gas-phase infrared spectrum contained bands at 1285 (vs), 1260 (vs), 1245 (s), 1205 (s), 1135 (s), 880 (w), 850 (m), 735 (m), 715 (s), 535 (vw), and 500 (vw) cm^{-1}. The mass spectrum at 70 eV does not contain a parent peak but a

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(3) B. Cohen, T. R. Hooper, D. Hugill, and R. D. Peacock, *Nature (London)*, **207**, 748 (1965); B. Cohen, T. R. Hooper, and R. D. Peacock, *Chem. Commun.*, 32 (1966).

(4) O. Glemser, *Angew. Chem., Int. Ed. Engl.*, **2**, 530 (1963).

(5) E. J. Barber, L. L. Burger, and G. H. Cady, *J. Amer. Chem. Soc.*, 73, 4241 (1951).

(6) A. F. Merrill, F. F. Detoro, and L. A. Bigelow, *ibid.*, **82**, 5827, (1960).

(7) W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1961, p 166.

(8) O. Glemser, *Prep. Inorg. React.*, **1**, 227 (1964).

strong P − 38^+(P − F_2) peak is observed. The most intense peak in the spectrum is that of the CF_3^+ ion.

Based on this work and other work in progress, it appears that for a given system there exists a temperature significantly higher than −196° where fluorine will not react with a delicate organic or inorganic reactant for thermodynamic and kinetic reasons. Just above that temperature, there may be a region in which the reaction rate may be controlled solely by careful control of the temperature. This would suggest that in certain cases one may be able to use pure fluorine at 1 atm pressure and control the reaction solely by temperature regulation. Cryogenic control does extend the applications of the La-Mar direct fluorination process. The major by-products of the fluorination of hexamethylethane are partially fluorinated species rather than fragments, and yields considerably higher than 10% could be achieved by recycling the products, by automating the process, or by using a longer cold reactor.

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N. J. Maraschin, R. L. Lagow*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received July 21, 1972

Structure of a New Isopolymolybdate–Cyclophosphazene Complex

Sir:

We report the first identification and structure analysis of the [$Mo_6O_{19}^{2-}$] anion, together with the first X-ray structure proof of a ring-protonated dimethylaminocyclotriphosphazene cation. The anion structure resolves the question of bonding in this and related species.

Hexakis(dimethylamino)cyclotriphosphazene, [$NP(NMe_2)_2]_3$, reacts with molybdenum trioxide in boiling water to give a yellow-green, water-insoluble, crystalline material (I). Conductance measurements of dilute acetonitrile solutions indicated that I was a strong electrolyte. Microanalysis followed by an X-ray single-crystal determination of this compound has shown that the correct formulation for I is $[HN_3P_3(NMe_2)_6^+]_2[Mo_6O_{19}^{2-}]$. Crystals of I, grown as prisms from a dichloromethane–hexane solvent mixture, were monoclinic, space group $P2_1/c$, a = 13.571 (13), b = 10.966 (11), c = 21.069 (19) Å; β = 108.36 (10)°; and Z = 2. Intensity data were collected on a Picker FACS-I system using Mo Kα radiation. The structure was solved by Patterson and Fourier methods using the 3126 unique observed reflections collected up to 2θ = 47.5°. Least-squares refinement of the atomic positional and thermal parameters for all but the methyl hydrogen atoms gave R = 0.030.

The molecular arrangement within each cation unit is shown in Figure 1. The bond distances within the six-membered ring are as follows: N(1)–P(1), 1.675 (5); P(1)–N(2), 1.563 (5); N(2)–P(2), 1.597 (5); P(2)–N(3), 1.599 (5); N(3)–P(3), 1.560; P(3)–N(1), 1.662 (5) Å. The difference Fourier map clearly revealed a hydrogen atom bonded to a ring nitrogen atom with the N(1)–H(N1) bond distance equal to 0.86 (6) Å. The six exocyclic P–N bonds had a mean length of 1.640 Å (range 1.623–1.658 Å) and the 12 N–C bonds of the amine groups had a mean length of 1.46 Å (range 1.43–1.47 Å). The principal bond angles are shown in the figure. The 12 N(ring)–P–N(exo) bond angles were in the range of 105.4–117.1° with a mean value of 110.1°. The ring adopts a highly distorted chair configuration. The displacements of the ring atoms from the least-squares plane were as follows: N(1), −0.08; P(1), 0.11; N(2), −0.09; P(2), 0.03; N(3), 0.00; P(3), 0.03 Å. The combined results confirm that the site of protonation is a ring nitrogen rather than an exocyclic nitrogen atom.[1] The ring hydrogen atom is directed toward one of the oxygen atoms of the molybdate anion, the distance H(N1)–O is 2.03 (6) Å and the angle N(1)–H(N1)–O is 172 (6)°.

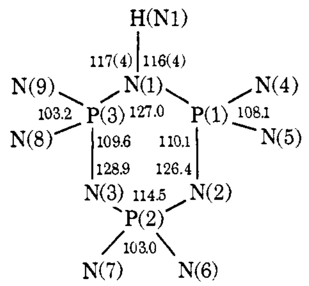

Figure 1. Molecular geometry and bond angles for the phosphazadiene cation. The standard deviations for the bond angles are 0.4° unless otherwise indicated.

The anion [$Mo_6O_{19}^{2-}$] is a new member of the group of discrete isopolymolybdate anions. Its structure can be considered as an octahedral array of molybdenum atoms with an oxygen atom O_a bonded to each molybdenum and pointing away from the center of the octahedron, an oxygen O_b spanning each edge and thus joining two molybdenum atoms, and one oxygen O_c at the center of the octahedron. Alternatively, the structure can be visualized as formed from six MoO_6 octahedra that have condensed so that they all share a common vertex. A similar structure has been proposed[2,3] for $Nb_6O_{19}^{8-}$ on the basis of the metal atom locations. The structure can also be considered as a subunit of the $V_{10}O_{28}^{6-}$ structure.[4] The central oxygen atom lies at the origin of the unit cell at an inversion center. The mean bond distances, bond angles, and ranges (in parentheses) for the atoms in the asymmetric unit are as follows: Mo–O_a, 1.678 Å (1.676–1.679); Mo–O_b, 1.928 (1.856–2.007); Mo–O_c, 2.319 (2.312–2.324); Mo–Mo, 3.274 (3.258–3.288); Mo–O_c–Mo, 89.8° (89.4–90.1); Mo–O_b–Mo, 116.5° (116.3–116.8); O_c–Mo–O_a, 177.8° (176.5–179.7). The standard deviations are 0.005 Å for the individual bond distances and 0.4° for the individual bond angles.

An optical spectrum believed to originate from the $Mo_6O_{19}^{2-}$ ion has been reported elsewhere,[5] with maxima at 222, 255, and 324 nm. Compound I in acetonitrile shows maxima at 257 and 325 nm with ϵ values of 6120 and 3080, respectively. This isolation

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