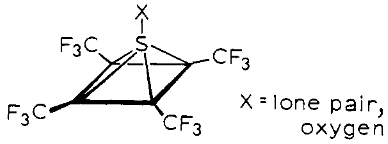
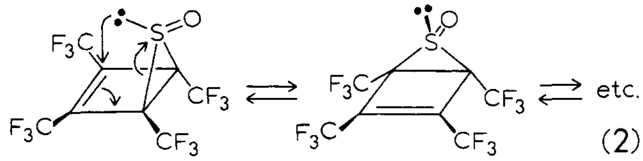
via a C_{4v} intermediate or transition state **3**,[6] cannot be ruled out on the basis of our current DNMR data (Figure 1). On the other hand, analogy to nondegenerate rearrangements of thiirane oxides favors the peripheral route for exchange.[6]



3

It has been proposed that the sulfoxide **2** rearranges via a pseudopericyclic [1,3]-sigmatropic shift (C_s transition state) in which bonding and nonbonding atomic orbitals at sulfur simultaneously interchange roles, as depicted below (eq 2).[6] The extraordinarily low activation enthalpy is consistent with this mechanism, for which the molecular geometry is admirably suited.[7]



(2)

Since the Dewar thiophene **1** likewise has an endo-oriented electron pair on sulfur, one may ask whether its automerization is also pseudopericyclic. If instead the reaction were to proceed via a singlet biradical formed by C–S homolysis, the activation enthalpy should be more than double the experimental value of 18.8 kcal/mol. Direct formation of a triplet by C–S homolysis cannot be so lightly dismissed, however, because (1) there is good evidence that such a triplet from thiirane itself is remarkably low-lying (~40 kcal/mol);[9] (2) allylic stabilization of the T_1 state of **1** could drop its energy still farther; and (3) the significantly negative activation entropy for automerization of **1** could be interpreted in terms of a spin-forbidden process. Nonetheless, the experimental $\Delta H^{\ddagger}$ is probably too small to accommodate a stepwise rearrangement mechanism.[10,11]

Hence we tentatively favor the concerted, pseudopericyclic pathway[6] for automerization of **1** as well as **2**, despite the enormous disparity in rate between these processes ($k_2/k_1 \cong 3 \times 10^{10}$ at 25 °C).[13]

In order to test the importance of the lone pair on sulfur in these rearrangements, a logical next step would be a DNMR investigation of the sulfone derived from **1**. Unfortunately, synthesis of this compound has proved elusive. Future DNMR investigations of unsymmetrically substituted analogues of **1** and **2**, however, may provide a firm answer to the question of the rearrangement itinerary.

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(10) Heterolytic cleavage of the C–S bond in this perfluorinated molecule is rather unpalatable.

(11) Evidence has been presented that α-methallyl phenyl sulfide undergoes allylic rearrangement via a cyclic, zwitterionic intermediate with negatively charged sulfur.[12] Such an intermediate in the automerization of our highly strained, perfluorinated system does not seem likely.

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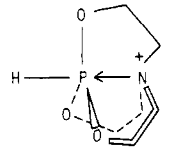
Characterization and Molecular Structure of S=P(OCH₂CH₂)₃N. Trigonal Planarity of Nitrogen

Sir:

Recently we reported the synthesis of the $[HP(OCH_2CH_2)_3N]^+$ (**1**) cation for which ^{31}P NMR spectral analysis suggested, and x-ray diffraction experiments confirmed, the tricyclic structure possessing a trigonal bipyramidal pentacoordinate phosphorus.[1]



1

Combination of the trivalent phosphorus cage in reaction 1 with elemental sulfur produces colorless sublimable crystals of the expected thiophosphate.[2]

$$P(NMe_2)_3 + (HOCH_2CH_2)_3N \xrightarrow{C_6H_6}$$

$$P(OCH_2CH_2)_3N \xrightarrow{S_8} \underset{\mathbf{2}}{S{=}P(OCH_2CH_2)_3N} \quad (1)$$

Although it was apparent from a comparison of the S=P stretching frequencies (618, 881 cm^{-1}) and ^{31}P NMR chemical shift (−61.0 ppm) of **2** with these parameters for S=P(OEt)$_3$ (614 cm^{-1}, 822 cm^{-1},[3] −68 ppm[4]) that the stereochemistry at phosphorus was probably normal, the nitrogen appeared to be considerably less reactive than expected. Quaternization with MeI at 40 °C in acetonitrile, for example, took 20 h whereas only 20 min was required for $N(CH_2CH_2OH)_3$ under the same conditions.

It therefore became of interest to undertake the molecular

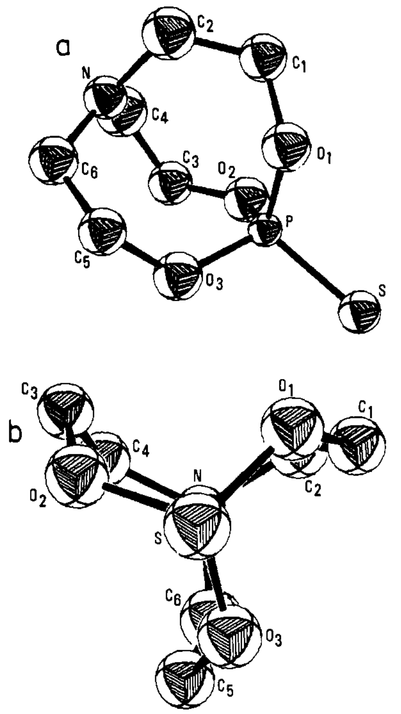


Figure 1. Computer drawing of 1-sulfo-2,8,9-trioxa-1-phospha-5-azabicyclo[3.3.3]undecane (**2**). The stereochemistries of nitrogen and phosphorus are emphasized in perspective (a) while the conformation of the bridging moieties is revealed in (b).

structure determination of this new cage molecule by x-ray diffraction techniques. Crystals of **2** were grown from a CH_2Cl_2 solution by slow evaporation or by vapor diffusion of hexane into a methylene chloride solution of **2** in a closed container. The crystals were found to belong to the orthorhombic crystal class with $a = 12.231$ (2), $b = 6.590$ (1), and $c = 11.284$ (2) Å and four molecular units of **2** per unit cell. Systematic extinctions ($h0l$ absent if $h = 2n + 1$, $0kl$ absent if $l = 2n + 1$) identified the space group as $Pca2_1$ or $Pcam$. The latter possibility was excluded during refinement.

A syntex $P2_1$ computer-controlled four-circle diffractometer was used to measure 755 unique reflection intensities inside a 2θ sphere of 114° with Cu $K\alpha$ radiation (1.5418 Å). Of these, 631 were judged observed after correction for Lorentz, polarization, and background effects ($F_o \geq 3\sigma(F_o)$).

Routine application of direct methods using MULTAN[5] produced the positions of sulfur, phosphorus, and the three oxygens in the first phased E synthesis. Refinement[6] of these parameters and subsequent electron density calculations[6] located the rest of the non-hydrogen atoms. Isotropic and anisotropic least-squares calculations proceeded uneventfully to conventional agreement factors of $R = 0.068$ and $R_w = 0.076$. All hydrogen positions were found in difference F syntheses.[6] Final full-matrix least-squares refinements gave final values of $R = 0.057$ and $R_w = 0.063$. Fractional coordinates, thermal parameters, and observed and calculated structure factors for this model are listed in the supplementary material to be found in the microfilm edition; see the paragraph at the end of this paper regarding supplementary material. Computer drawings[6] of this model are shown in Figure 1 and the intramolecular bond distances and angles are listed in Table I. No abnormally short intermolecular contacts were observed.

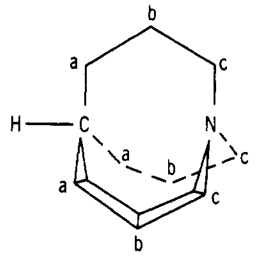
Table I. Intramolecular Bond Distances and Angles for $S{=}P(OCH_2CH_2)_3N$[a]

Distances (Å)		Angles (deg)	
P-S	1.933 (3)	S-P-0(1)	110.7 (3)
P-0(1)	1.568 (7)	S-P-0(2)	110.6 (3)
P-0(2)	1.609 (7)	S-P-0(3)	111.2 (2)
P-0(3)	1.548 (7)	0(1)-P-0(2)	106.2 (4)
0(1)-C(1)	1.528 (12)	0(1)-P-0(3)	110.0 (4)
0(2)-C(3)	1.513 (11)	0(2)-P-0(3)	108.0 (4)
0(3)-C(5)	1.492 (12)	0(1)-C(1)-C(2)	116.0 (8)
C(1)-C(2)	1.537 (14)	0(2)-C(3)-C(4)	116.6 (8)
C(3)-C(4)	1.538 (14)	0(3)-C(5)-(6)	117.1 (8)
C(5)-C(6)	1.589 (14)	P-N-C(2)	84.1 (5)
C(2)-N	1.460 (14)	P-N-C(4)	85.6 (5)
C(4)-N	1.424 (14)	P-N-C(6)	84.3 (5)
C(6)-N	1.466 (14)	P-0(1)-C(1)	124.3 (6)
		P-0(2)-C(3)	126.1 (6)
		P-0(3)-C(5)	127.6 (7)
		N-C(2)-C(1)	118.3 (8)
		N-C(4)-C(3)	117.9 (7)
		N-C(6)-C(5)	116.5 (8)
		C(2)-N-C(4)	119.5 (8)
		C(2)-N-C(6)	116.2 (9)
		C(4)-N-C(6)	121.8 (9)
		S-P-N	179.2 (4)

[a] Numbering of the atom corresponds to that in Figure 1.

In contrast to **1** wherein the nitrogen is almost tetrahedral (av CNC angle = 113.3°), it is very nearly trigonal planar in **2** (av CNC angle = 119.2°). Furthermore, the phosphorus stereochemistry in **1** is trigonal bipyramidal while in **2** it is tetrahedral (av OPO angle = 108.1°). These observations, coupled with the large P-N distance in **2** (3.132 Å) compared to **1** (1.986 Å), allow the tentative conclusion that there is little if any interaction between the nitrogen lone pair and the thiophosphate moiety. Thus compared to the proton in **1** the sulfur atom in **2** is not sufficiently electron withdrawing to allow phosphorus to polarize the nitrogen p lone pair into an sp^3 configuration.

The planar nitrogen in **2** is probably more steric in origin than electronic. From chemical and spectroscopic studies of manxine (**3**) it has been inferred that bridgehead angles are opened substantially by interactions of hydrogens on carbons a and b and on carbons c and b of different bridge pairs.[7] Evidence of such strain is also found in the hydrochloride salt of **3** whose molecular structure revealed average CNC and NCC angles of 115.5 and 117.4°, respectively, and average CCC angles ranging from 114.2 to 120.0°.[8] In **2**, the absence of hydrogens on the three oxygens along with the flexibility of oxygen in organophosphorus compounds[9] allows phosphorus to retain its normal angles. The nitrogen bridgehead stereochemistry, on the other hand, is subject to hydrogen interactions from carbons b and c.



3

Acknowledgment. J.G.V. thanks the National Science Foundation for generous grant support of this research.

Supplementary Material Available: fractional coordinates, thermal parameters, and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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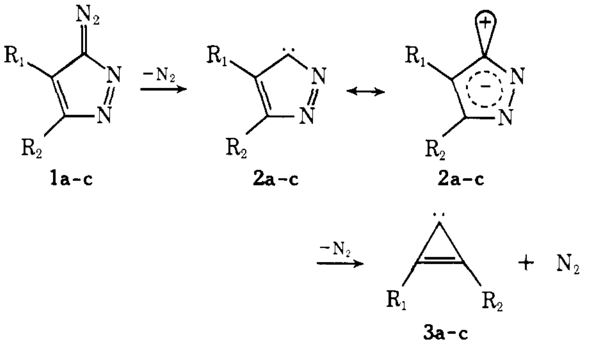
3-Diazopyrazoles: Sources of Unusual Carbenes and Dipolar Reagents

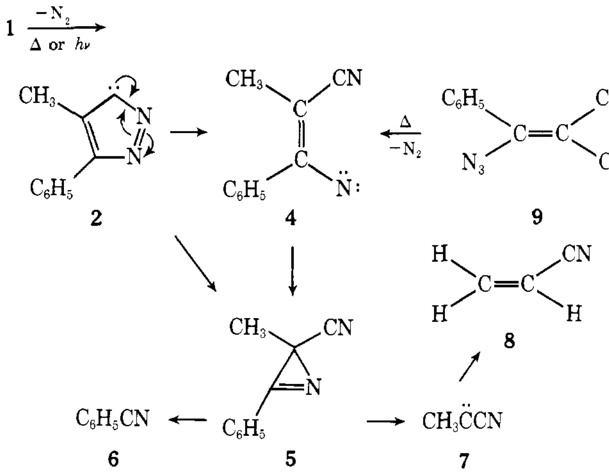
Sir:

Knowledge of the carbenic chemistry of 3-diazopyrazoles[1a] is limited to photolytic conversions of 3-benzoyl-5-diazo-4-phenylpyrazole in aqueous acetone and in benzene to 3(5)-benzoyl-4-phenylpyrazole and 3-benzoyl-4,5-diphenylpyrazole, respectively. There is no information relative to 3-diazopyrazoles as dipolar reagents.[1b] A study is presently summarized of decomposition and dipolar reactions of 3-diazopyrazoles **1a-c** and novel behavior of 3*H*-pyrazolylidenes **2a-c.** Carbenes **2a-c** might be expected to behave as highly electrophilic singlets and as possible sources of cyclopropenylidenes **3a-c** (eq 1).[1c] It has now been observed that 3*H*-pyrazolylidenes (a) isomerize to 2*H*-azirines (eq 2), (b) are capturable prior to carbenic rearrangement by insertion into C-H bonds (eq 3), (c) react with benzene by substitution and by ring expansion/sigmatropic rearrangement processes (eq 4 and 5), and (d) cleave ethers by nucleophilic attack on oxygen to give 1,2- and 1,3-adducts (eq 6). Of further note is that 3-diazopyrazoles undergo dipolar reactions with electron-rich olefins to yield 1,4- instead of 1,3-adducts (eq 7).



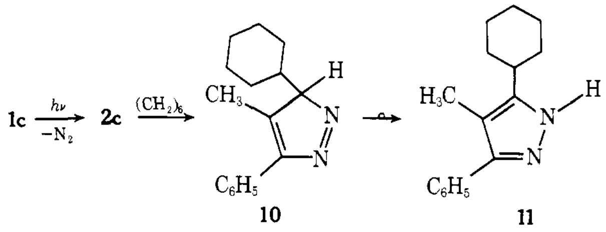
(1)

3-*tert*-Butyl-5-diazopyrazole (**1a**), 3-diazo-5-phenylpyrazole (**1b**), and 3-diazo-4-methyl-5-phenylpyrazole (**1c**), prepared by diazotization of the corresponding amines[2a-c] with nitrous acid in fluoboric or hydrochloric acids and neutralization with aqueous carbonates, are sensitive solids but, with care, are easily manipulated.[2d] Pyrolysis of **1c** at 250 °C (60 mmHg) yields 2-cyano-2-methyl-3-phenyl-2*H*-azirine (**5,** > 60%),[3a,b] benzonitrile (**6,** 10%), and acrylonitrile (**8**). Photolysis of **1c**[3c] in cyclohexane also gives **5** (competitive solvent insertion is to be subsequently discussed). There was no evidence for cyclopropenylidene **3c** in these experiments. The structure of **5** is established from its spectra[3b] and by comparison with an identical product obtained by thermolysis of β-azido-α-methylcinnamonitrile (**9**).[3d] Conversion of **1c** to **5** possibly occurs by ring-opening of **2c** to nitrene **4** and subsequent heterocyclization or/and by concerted rearrangement of **2d.** Fragmentation products **6** and **8** may result from carbenic collapse of **5** (eq 2) and hydrogen migration in the methylcyanocarbene (**7**) generated.[4] At 175-300 °C (>50 mmHg) **1a** and **1b** yield 3-*tert*-butyl-2-cyano-2*H*-azirine (>35%)[5a] and 2-cyano-3-phenyl-2*H*-azirine (65%),[5b] respectively. Decomposition of 3-diazopyrazoles to 2*H*-azirines appears to be general and of value synthetically.



(2)

Irradiation of **1c**[3c] in cyclohexane yields 3(5)-cyclohexyl-4-methyl-5(3)-phenylpyrazole[3a,6a] (**11,** 60%; eq 3) and azirine **5** (15%). Along with generation of **5** photolytically, this experiment reveals that **2c,** apparently a discrete intermediate, inserts into cyclohexane to give **11,** presumably after 1,5-sigmatropic isomerization of **10.** Pyrazolylidene **2a,** produced thermally or photolytically[3c] from **1a,** reacts with benzene to yield 3(5)-*tert*-butyl-5(3)-phenylpyrazole[3a,6b] (**14,** 85-90%) and 2-*tert*-butylpyrazolo[3,2-*a*]azocine[3a,6c] (**16,** 10%), a derivative of a new heterocyclic system. Formation of pyrazole **14** and azocine **16,** assigned from their analyses and spectra, is rationalized by eq 4 and 5 and is formally analogous to photolytic conversion of 5-diazo-1,2,3-triphenyl-1,3-cyclopentadiene in benzene[6d] to 1,2,3,4-tetraphenyl-1,3-cyclopentadiene and 9,10,11-triphenyl-2,4,6,8,10-bicyclo[6.3.0]undecapentaene. The transformation of significance is the apparent 1,5-sigmatropic[6e] rearrangement of **15** as led by pyrazolo nitrogen rather than carbon, and, on the basis of the mechanistic aspects of eq 4 and 5, reactions of **1a** with benzenes containing electron-withdrawing substituents are predicted to give increased conversions to pyrazolo[3,2-*a*]azocines.



(3)