alone (cases 8 vs. 1 and 9 vs. 2). *O*-Acetyl-II was isolated from the III + II + PNPA experiment. Further, the enhancement of k_{deacyl}, relative to k^{III}_{deacyl}, is greater with micellar IV than with the 1:1 III + II comicelle (cf. cases 3, 8, and 1, and 4, 9, and 2). The additional enhancement can probably be ascribed to intramolecular N-to-O acyl transfer. Finally, the reaction of PNPA with micellar *O*-acetyl-IV[15] affords a spectroscopically observable *N,O*-diacetyl derivative. Because free hydroxyl groups are unavailable for either intermolecular or intramolecular N-deacylation of this intermediate, k_{deacyl} is small and similar to that of *N*-acetyl-III (cases 5 vs. 1).

The weight of assembled evidence thus leads us to prefer mechanism 2 for the cleavage of *p*-nitrophenyl esters by micellar IV; independent studies by Tonellato afford the same conclusion.[20] Although cooperative catalysis was not observed with IV, we did uncover an extremely facile, sequential process, in which a micellar imidazole-functionalized surfactant cleaves an ester, then rapidly acylates a proximate hydroxyl group. The catalytic advantage of the first step ($k_\psi^{max}/k_o^{buffer}$) is 930.[10] Because this is the rate determining step of the sequence, it confers an effective catalytic advantage of ~37 on the acylation of the hydroxyl function, relative to the acylation of pure micellar II by PNPA.[10] We are continuing our studies of multifunctional micellar catalysts.[21]

Acknowledgments. We are grateful to the National Science Foundation and to the Public Health Service (Research Grant CA-14912 from the National Cancer Institute) for financial support. R.A.M. thanks the Dyson Perrins Laboratory, University of Oxford for its hospitality.

References and Notes

(1) (a) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, N.Y., 1975; (b) E. H. Cordes, Ed., "Reaction Kinetics in Micelles", Plenum Press, New York, N.Y., 1973; (c) C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", Wiley-Interscience, New York, N.Y., 1973; (d) C. A. Bunton, *Prog. Solid State Chem.*, **8**, 239 (1973); (e) E. H. Cordes and C. Gitler, *Prog. Biorg. Chem.*, **2**, 1 (1973); (f) I. V. Berezin, K. Martinek, and A. K. Yatsimirski, *Russ. Chem. Rev.*, **42**, 787 (1973); (g) for an early, critical view, see H. Morawetz, *Adv. Catal.*, **20**, 341 (1969).

(2) For a review, see ref 1a, pp 169–189.

(3) (a) E. Zeffren and P. L. Hall, "The Study of Enzyme Mechanisms", Wiley-Interscience, New York, N.Y., 1973, pp 167–193; (b) W. P. Jencks in "Chemical Reactivity and Biological Role of Functional Groups in Enzymes", R. M. S. Smellie, Ed., Academic Press, New York, N.Y., 1970, p 59ff; (c) A. D. B. Malcolm and J. R. Coggins, *Ann. Rep. Chem. Soc.*, **71B**, 540–544 (1974); (d) D. M. Blow, *Acc. Chem. Res.*, **9**, 145 (1976).

(4) T. H. Fife, *Adv. Phys. Org. Chem.*, **11**, 1 (1975).

(5) (a) C. A. Bunton, L. Robinson, and M. Stam, *J. Am. Chem. Soc.*, **92**, 7393 (1970); (b) M. Chevion, J. Katzhendler, and S. Sarel, *Isr. J. Chem.*, **10**, 975 (1972); (c) G. Meyer, *Tetrahedron Lett.*, 4581 (1972); (d) G. Meyer, *C. R. Acad. Sci., Ser. C*, **276**, 1599 (1973); (e) C. A. Bunton and L. G. Ionescu, *J. Am. Chem. Soc.*, **95**, 2912 (1973); (f) V. Gani, C. Lapinte, and P. Viout, *Tetrahedron Lett.*, 4435 (1973); (g) K. Martinek, A. A. Levashov, and I. V. Berezin, *ibid.*, 1275 (1975); (h) C. A. Bunton and M. McAneny, *J. Org. Chem.*, **41**, 36 (1976); (i) C. A. Bunton and S. Diaz, *ibid.*, **41**, 33 (1976).

(6) The imidazole moiety can be supplied as an hydrophobic acylhistidine or benzimidazole solubilized by a "carrier" micelle: (a) A. Ochoa-Solano, G. Romero, and C. Gitler, *Science*, **156**, 1243 (1967); (b) C. Gitler and A. Ochoa-Solano, *J. Am. Chem. Soc.*, **90**, 5004 (1968); (c) P. Heitmann, R. Husung-Bublitz, and H. J. Zunft, *Tetrahedron*, **30**, 4137 (1974); (d) A. P. Osipov, K. Martinek, A. K. Yatsimirski, and I. V. Berezin, *Dokl. Akad. Nauk SSSR*, **215**, 914 (1974); (e) K. Martinek, A. P. Osipov, A. K. Yatsimirski, V. A. Dadali, and I. V. Berezin, *Tetrahedron Lett.*, 1279 (1975); (f) K. Martinek, A. P. Osipov, A. K. Yatsimirski, and I. V. Berezin, *Tetrahedron*, **31**, 709 (1975). Or, the imidazole moiety can be part of the surfactant itself: (g) W. Tagaki, M. Chigira, T. Ameda, and Y. Yano, *J. Chem. Soc., Chem. Commun.*, 219 (1972); (h) J. M. Brown and C. A. Bunton, *ibid.*, 969 (1974); (i) J. M. Brown, C. A. Bunton, and S. Diaz, *ibid.*, 971 (1974); (j) D. G. Oakenfull and D. E. Fenwick, *Aust. J. Chem.*, **27**, 2149 (1974); (k) U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, 771 (1976).

(7) (a) A macrocyclic *oxime* solubilized in micellar III catalyzes the cleavage of PNP palmitate with apparent functional group cooperativity, but the imidazole group is the nucleophile: J. Sunamoto, H. Okamoto, H. Kondo, and Y. Murakami, *Tetrahedron Lett.*, 2761 (1975). (b) *N*-Lauryl-4-imidazolylcarbohydroxamic acid solubilized in micellar I-Br cleaves PNPA with *O*-acetylation two–three times faster than *N*-laurylbenzohydroxamic acid-I-Br, suggesting chymotropysin-like cooperativity of imidazole and hydroxamic acid moieties: T. Kunitake, Y. Okahata, and T. Sakamoto, *Chem. Lett.*, 459 (1975). (c) Several multifunctional polymeric[8] or cyclodextrin[9] catalysts have been studied.

(8) N. Ise, T. Okubo, H. Kitano, and S. Kunugi, *J. Am. Chem. Soc.*, **97**, 2882 (1975); C. G. Overberger and Y. Okamoto, *Macromolecules*, **5**, 363 (1972); C. G. Overberger and J. C. Salamone, *Acc. Chem. Res.*, **2**, 217 (1969).

(9) Y. Iwakura, K. Uno, F. Toda, S. Onozuka, K. Hattori, and M. L. Bender, *J. Am. Chem. Soc.*, **97**, 4432 (1975); D. W. Griffiths and M. L. Bender, *Adv. Catal.*, **23**, 209 (1973); F. Cramer and G. Mackensen, *Angew. Chem., Int. Ed. Engl.*, **5**, 601 (1966); *Chem. Ber.*, **103**, 2138 (1970).

(10) R. A. Moss, R. C. Nahas, S. Ramaswami, and W. J. Sanders, *Tetrahedron Lett.*, 3379 (1975).

(11) k_ψ^{max} is the maximal pseudo-first-order rate constant for *p*-nitrophenolate release (determined at [surfactant] at which substrate is completely bound).

(12) Im = 4-imidazolyl.

(13) Conditions: [surfactant] = 5.0×10^{-3} M; [substrate] = 2.0×10^{-4} M; pH 8.0, 0.4 M phosphate buffer, 25 °C. Unless otherwise specified, these conditions apply to all kinetic experiments. Cmc's were III, 7.9×10^{-5} M and IV, 6.8×10^{-5} M, in 0.01 M phosphate buffer.[10]

(14) Conditions: [PNPA] = 1.0×10^{-3} M and [IV] = 5.0×10^{-3} M in 50 ml of 1.1 M aqueous KCl; titrant, 1.11×10^{-1} M aqueous NaOH, pH-stat-titrimeter at pH 8.0. After the consumption of 1 equiv of base, acidification (HCl to pH 1.5) and lyophilization of the product, followed by ethereal washing, extraction with 3:1 acetone–methanol, and precipitation with ether, afforded a mixture of IV·HCl and *O*-acetyl-IV·HCl,[15] the IR spectrum of which was superimposable on that of an authentic 84:16 (the anticipated molar ratio) mixture; cf. especially, the ester carbonyl band at 1740 cm^{-1}.

(15) Cf. U. K. Pandit and T. C. Bruice, *J. Am. Chem. Soc.*, **82**, 3386 (1960); satisfactory spectral and analytical data were obtained.

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2d ed, Wiley, New York, N.Y., 1961, pp 166–169.

(17) The apparent k_{acyl} is also depressed upon dilution of IV with I (factor of 2.4) because PNPA is bound to "inert" regions of the comicelle. But k_{deacyl} is more sharply diminished, leading to an observable accumulation of *N*-acetyl-IV.

(18) Parallel experiments with PNPH indicate a 4.5-fold decrease of k_{deacyl} upon fivefold dilution with I, cases 7 vs. 4. Here, however, there is a proportionate decrease in k_{acyl}.

(19) This is not surprising; intramolecular deacylation of *N*-acyl-IV requires an eight-membered cyclic transition state.

(20) U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, in press. We are grateful to Professor Tonellato for exchanges of correspondence and manuscripts.

(21) The above work was presented at the "International Symposium on Micellization, Solubilization, and Microemulsions", 7th Northeast Regional Meeting of the American Chemical Society, Albany, N.Y., Aug 10, 1976.

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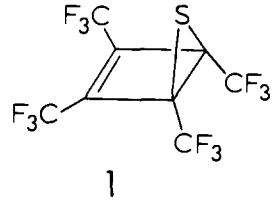
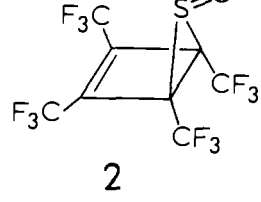
Automerization of a Dewar Thiophene and Its *exo*-*S*-Oxide. A Dramatic Contrast

Sir:

As the only known Dewar isomer of a thiophene, perfluorotetramethyl(Dewar thiophene) (**1**)[1] is an especially interesting compound both from structural and dynamical points of view. This report concerns ^{19}F DNMR studies of **1** and its *exo*-*S*-oxide (**2**) which reveal a marked difference between the rates of intramolecular exchange in **1** and **2**.



1



2

Examination of the ^{19}F DNMR spectrum (56.4 MHz) of **1** (1.0 M in 1,2,4-trichlorobenzene) at 94 °C (Figure 1) shows two quartet resonances at 13.10 and 15.99 ppm ($^5J_{FF}$ = 2 Hz) downfield from external trifluoroacetamide, consistent with the structure of **1**. When the temperature is raised (Figure 1), the ^{19}F DNMR spectrum undergoes broadening and coalescence near 190 °C (Figure 1) characteristic of an increasing rate of exchange of trifluoromethyl groups between different

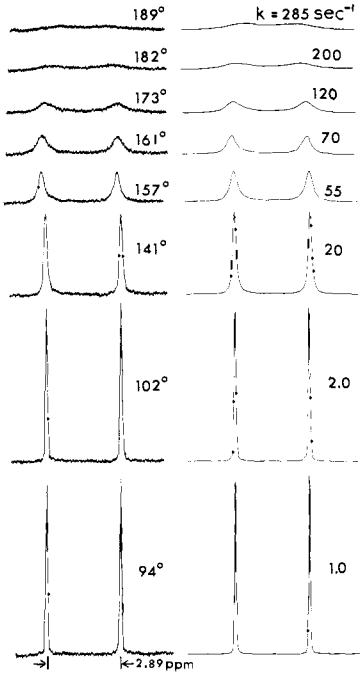
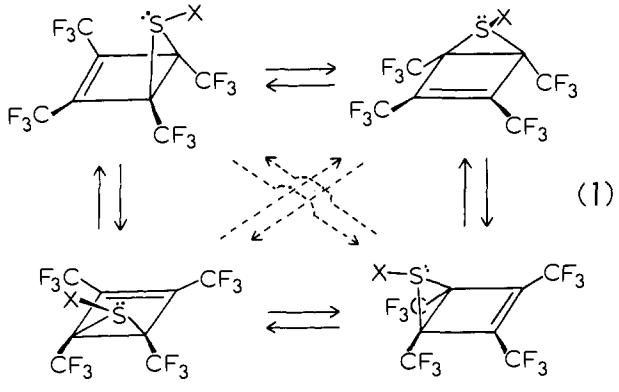


Figure 1. The experimental ^{19}F DNMR spectra (56.4 MHz) of **1** (1.0 M in 1,2,4-trichlorobenzene) at various temperatures and theoretical ^{19}F DNMR spectra calculated using a two-site exchange model with a trifluoromethyl group at each site and $^5J_{FF} = 2$ Hz (k = first-order rate constant for disappearance of a trifluoromethyl group from one site).



sites (e.g., eq 1; X = lone pair). The trifluoroacetamide ^{19}F singlet resonance remains sharp ($W_{1/2} < 1$ Hz) over the temperature range from 94 to 189 °C. Theoretical ^{19}F DNMR spectra were calculated using a dynamical model having one trifluoromethyl group at each of two sites ($^5J_{FF} = 2$ Hz) and employing a local substantially modified version of computer program DNMR3.[2] Theoretical spectra calculated as a function of the rate of trifluoromethyl group exchange are illustrated in Figure 1 and activation parameters derived from the complete DNMR line shape analyses are $\Delta H^{\ddagger} = 18.8 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -7.7 \pm 0.8$ cal/mol-deg, and $\Delta G^{\ddagger} = 22.1 \pm 0.1$ kcal/mol at 157.0 °C.

Remarkably, aromatization of **1** to perfluorotetramethylthiophene is too slow even at ~190 °C to interfere significantly with our study of the degenerate rearrangement.[3] The great resistance this molecule offers to opening of the bridging bond stands in striking contrast to the lability of the parent hydrocarbon, bicyclo[2.1.0]-2-pentene ($t_{1/2} = 4$ h at 34 °C),[4] whose ring opening does *not* generate an aromatic system. The Dewar thiophene's impressive stability with regard to aromatization is another manifestation of the "perfluoroalkyl effect".[5]

Examination of the ^{19}F DNMR spectrum of **2**,[6] the exo sulfoxide derived from **1** (~1.6 M in 80% $CHCl_2F$/20% $CHClF_2$, v/v), at −78.5 °C (Figure 2) shows a sharp singlet resonance (21 ppm downfield from the center of the $CHCl_2F$ doublet) in significant contrast to the ^{19}F DNMR spectrum of **1** at 94 °C (Figure 1). When the temperature is lowered, the ^{19}F DNMR spectrum of **2** broadens and is separated at −151 °C into two singlets of *equal area* (albeit differentially broadened) which are 2.82 ppm apart (Figure 2). At temperatures below −150 °C, the lowfield singlet broadens at a significantly more rapid rate than the upfield singlet (Figure 2). From −78 to −150 °C, the observed spectral behavior is consistent with the slowing of a process which equilibrates the trifluoromethyl groups (e.g., eq 1; X = O). The observation of two singlets of *equal area* at −151 °C (Figure 2) is also consistent with the *static* structure of **2**. The differential broadening of the low-field singlet at low temperatures is best rationalized in terms of a second rate process in **2** beginning to slow down on the ^{19}F DNMR time scale. The only rate process left is of course simple rotation of individual trifluoromethyl groups. The greater degree of broadening of the lowfield singlet may reflect a higher barrier to CF_3 rotation and/or larger ^{19}F DNMR chemical shift differences in the static trifluoromethyl groups in that particular environment as compared to the trifluoromethyl groups giving the upfield singlet.

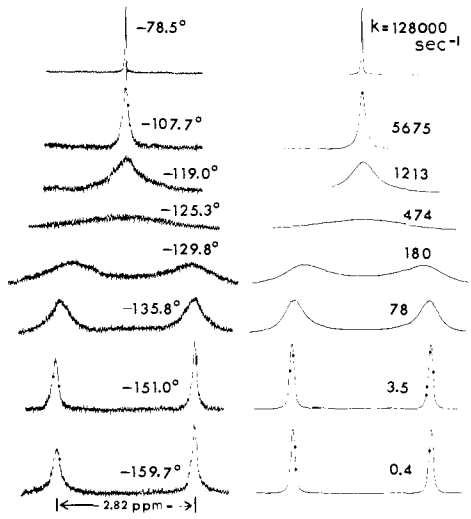
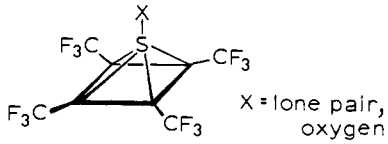


Figure 2. The experimental ^{19}F DNMR spectra (56.4 MHz) of **2** (~1.6 M in 80% $CHCl_2F$/20% $CHClF_2$) at various temperatures and theoretical ^{19}F DNMR spectra calculated using a two-site exchange model with a trifluoromethyl group at each site and $^5J_{FF} = 2$ Hz (k = first-order rate constant for disappearance of a trifluoromethyl group from one site).

Complete ^{19}F DNMR line shape analyses of the spectra for **2** were performed using a DNMR model strictly analogous to **1**, i.e., a two-site exchange with a trifluoromethyl group at each site ($^5J_{FF} = 2$ Hz). Based on our experience with other fluorinated compounds of comparable geometry, a systematic decrease in T_2 with decreasing temperature was also introduced into the theoretical calculations. Hence, the spin-spin coupling is not resolved in the theoretical spectra corresponding to very low temperatures due to the short T_2 values employed (Figure 2). The DNMR model used does not of course account for the apparent intervention of a second rate process (i.e., CF_3 rotation), but the differential broadening associated with this phenomenon above −150 °C and into the coalsecence region is minor and will contribute negligibly to the total line shape. However, the discrepancy between theoretical and experimental line shapes is indeed more severe at temperatures below −151 °C (Figure 2). Activation parameters for trifluoromethyl group exchange in **2** derived from complete DNMR line shape analyses (Figure 2) are $\Delta H^{\ddagger} = 6.6 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = -0.5 \pm 0.6$ cal/mol-deg, and $\Delta G^{\ddagger} = 6.7 \pm 0.1$ kcal/mol at −135.8 °C.

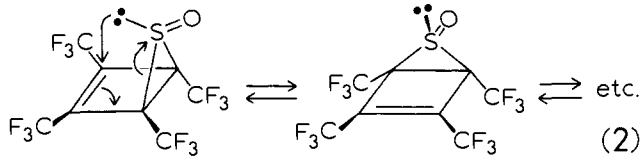
With regard to the mechanism of exchange in **1** and **2**, trifluoromethyl exchange along the dotted diagonals in eq 1, e.g.,

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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References and Notes

(1) H. A. Wiebe, S. Braslavsky, and J. Heicklen, *Can. J. Chem.*, **50**, 2721 (1972).
(2) The original version of DNMR3 was written by D. A. Kleier and G. Binsch, *J. Magn. Reson.*, **3**, 146 (1970); Program 165, Quantum Chemistry Program Exchange, Indiana University. Our local modifications are described in C. H. Bushweller, G. Bhat, L. J. Letendre, J. A. Brunelle, H. S. Bilofsky, H. Ruben, D. H. Templeton, and A. Zalkin, *J. Am. Chem. Soc.*, **97**, 65 (1975).
(3) The half-life for aromatization of the Dewar thiophene has been reported to be 5.1 h at 160 °C. Y. Kobayashi, I. Kumadaki, A. Ohsawa, and Y. Sekine, *Tetrahedron Lett.*, 1639 (1975).
(4) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem. Soc.*, **93**, 6145 (1971); D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969); J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968).
(5) D. M. Lemal and L. H. Dunlap, Jr., *J. Am. Chem. Soc.*, **94**, 6562 (1972).
(6) J. A. Ross, R. P. Seiders, and D. M. Lemal, *J. Am. Chem. Soc.*, **98**, 4325 (1976).
(7) Using overlap integrals based on Slater functions,[8] we estimate the overlap integral between the sulfur lone pair orbital in **2** (taken as sp^3) and each of the p orbitals of the C–C double bond to be ~0.06 prior to any distortion along the reaction coordinate.
(8) R. S. Mulliken, C. A. Rieke, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
(9) O. P. Strausz, H. E. Gunning, A. S. Denes, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **94**, 8317 (1972); E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *ibid.*, **90**, 7164 (1968).
(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.
(12) H. Kwart and J. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976). See also H. Kwart and N. Johnson, *ibid.*, **92**, 6064 (1970).
(13) Nondegenerate allylic and homollylic rearrangement of thiiranes has also been found to be very much slower than that of the corresponding sulfoxides. R. P. Seiders and D. M. Lemal, unpublished work.
(14) Alfred P. Sloan Research Fellow; Camille and Henry Dreyfus Teacher-Scholar.

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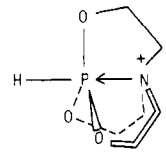
Characterization and Molecular Structure of $S{=}P(OCH_2CH_2)_3N$. Trigonal Planarity of Nitrogen

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]

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

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

2

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