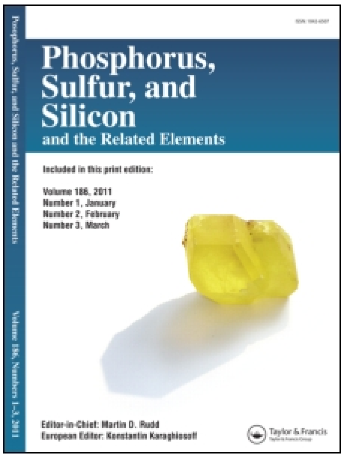

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A Multinuclear NMR Study of the Cycloaddition Reaction of $SNSAsF_6$ with the Phosphaalkyne $(CH_3)_3CCP$; REDUCTION OF THE 6π Cycloadduct 1,3,2,4-Dithiazophospholium $^+$

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A MULTINUCLEAR NMR STUDY OF THE CYCLOADDITION REACTION OF $SNSAsF_6$ WITH THE PHOSPHAALKYNE $(CH_3)_3CCP$; REDUCTION OF THE 6π CYCLOADDUCT 1,3,2,4-DITHIAZOPHOSPHOLIUM $(CH_3)_3C\overline{CPSNS}^+$

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Abstract The cycloaddition reaction of SNS^+ (as the AsF_6^- salt) with the phosphaalkyne $(CH_3)_3CCP$ gave $(CH_3)_3C\overline{CPSNS}^+$, the first example of any 1,3,2,4-dithiazophospholium heterocycle. Reduction of 6π $(CH_3)_3C\overline{CPSNS}^+$ in situ with $SbPh_3$ in the presence of Me_4NCl probably led to a new 7π 1,3,2,4-dithiazophospholyl $(CH_3)_3C\overline{CPSNS}^\bullet$ radical.

INTRODUCTION

The SNS^+ cation (as the AsF_6^- salt) has been shown[1,2] to undergo general quantitative symmetry allowed cycloaddition reactions with a variety of nitriles, alkynes, and alkenes. The kinetics[1] of these cycloadditions have shown that they are among the simplest of any 1,3-dipolar cycloadditions. It seemed almost certain that the cycloaddition chemistry of SNS^+ was extendable to other multiply unsaturated systems. In this paper, we report the reaction of $SNSAsF_6$ with the phosphaalkyne $(CH_3)_3CCP$ and the subsequent reduction of the product.

CYCLOADDITION OF $SNSAsF_6$ WITH THE PHOSPHAALKYNE $(CH_3)_3CCP$

The reaction of $SNSAsF_6$ (2.86 mmol) with $(CH_3)_3CCP$ (2.81 mmol) was performed in liquid SO_2 (2.82 g) in a 10 mm NMR tube at -60°C, and the product was characterized in situ by multinuclear NMR (^1H, ^{13}C, ^{14}N, ^{15}N, ^{31}P) spectroscopy[3] at the same temperature. $\delta(^{14}N)=37.5$ ppm ($\Delta\nu_{1/2}=790$ Hz); $\delta(^{15}N)=30.8$ ppm (singlet, $\Delta\nu_{1/2}=4.8$ Hz); $\delta(^{31}P)=389.2$ ppm (singlet); $\delta(^1H)=1.52$ ppm (singlet); and ^{13}C spectral data (δ (ppm), assignment): 237.5 (doublet, $^1J_{CP}=104.4$ Hz, $\overline{CPSNS}^+$), 43.2 (doublet, $^2J_{CP}=12.8$ Hz, tert-C), and 35.7 (doublet, $^3J_{CP}=7.0$ Hz, CH_3).

The NMR (^1H, ^{13}C, ^{31}P) resonances of the cycloadduct $(CH_3)_3C\overline{CPSNS}^+$ appear at lower field relative to those of $(CH_3)_3CCP$[4], characteristic of formation of the deshielding cation. The magnitude of $^1J_{PC}$ of $(CH_3)_3C\overline{CPSNS}^+$ (104 Hz) is greater than that of $(CH_3)_3CCP$ (38.5 Hz), characteristic of decrease in the CP bond order by formation of $\overline{CPSNS}^+$ heterocycle, indicating the presence of a C=P double bond. Our NMR results also quantitatively fit Eqn.1 and 2 which have been previously established[5] for the correlations of $\delta(^{31}P)$ of various =P- containing acyclic and heterocyclic compounds to $\delta(^{14}N)$ and $\delta(^{13}C)$ of the corresponding =N- (replacement of P by N) and =CH- (replacement of P by CH) moieties in analogous acyclic and heterocyclic compounds.

$$\delta(^{31}P)=1.33\delta(^{14}N) + 279 \tag{1}$$

$$\delta(^{31}P)=4.88\delta(^{13}C) - 422 \tag{2}$$

The multinuclear NMR spectroscopic studies showed that SNS^+ undergoes symmetry allowed cycloaddition reaction with $(CH_3)_3CCP$ to give a novel five-membered heterocyclic $(CH_3)_3C\overline{CPSNS}^+$ cation, which is the first example of any 1,3,2,4-dithiazophospholium heterocycle. The NMR studies also showed that the cycloadduct $(CH_3)_3C\overline{CPSNS}AsF_6$ undergoes decomposition at room temperature to give a complex mixture with almost all the phosphorus converted PF_6^-.

REDUCTION OF 1,3,2,4-DITHIAZOPHOSPHOLIUM $(CH_3)_3C\overline{CPSNS}^+$

The in situ reduction of $(CH_3)_3C\overline{CPSNS}^+$ (produced from the cycloaddition of $SNSAsF_6$ with $(CH_3)_3CCP$ at -60°C) with excess $SbPh_3$ in the presence of Me_4NCl at -40°C gave a radical species the ESR spectrum of which exhibited a 1:1:1 triplet presumably due to the coupling to ^{14}N (I=1) with g=2.0059 and a^N=1.14 mT. This is reasonably attributed to a new type of heterocyclic 7π 1,3,2,4-dithiazophospholyl $(CH_3)_3C\overline{CPSNS}^\bullet$ (cf. the previously known $(CH_3)_3C\overline{CNSNS}^{\bullet}$[6]) by comparison with various conjugated $SNS^\bullet$ moiety containing heterocyclic radicals (g=2.005-2.007, $a^N=1.10\pm0.03$)[7]. The a^P coupling was not observable even at -60°C. The difference between a^N and a^P values may be interpreted by comparison of the coefficients of p_π SOMO (STO-3G) on N (0.97) and P (0.08).

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4. NMR (^1H, ^{13}C, ^{31}P) spectral data for $(CH_3)_3CCP$: $\delta(^{31}P)=-69.2$ ppm (singlet); $\delta(^1H)=1.21$ ppm (doublet, $^4J_{HP}=0.88$ Hz); and ^{13}C spectral data (δ (ppm), assignment): 184.8 (doublet, $^1J_{CP}=38.5$ Hz, CP), 36.4 (doublet, $^2J_{CP}=18.2$ Hz, tert-C), and 31.3 (doublet, $^3J_{CP}=6.0$ Hz, CH_3). Also see ref.3.
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