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# SULFURIZATION OF 4,5,6-TRIPHOSPHA[3]RADIALENE

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**Abstract** Sulfurization reaction of a stable 4,5,6-triphospha[3]radialene led to the formation of the corresponding methylene(thioxo)phosphorane, which was isolated and characterized. The characteristic absorption maximum of the sulfurized compound in electronic spectrum was shifted toward the longer wavelength region relative to that of the triphospha[3]radialene. Desulfurization reaction of the sulfurized compound to 4,5,6-triphospha[3]radialene was also demonstrated.

Keywords Low-coordinated phosphorus compound; sulfurization; radialene

#### INTRODUCTION

Radialenes are organic compounds of considerable chemical interest due to their cyclic cross- $\pi$ -conjugated system.<sup>1</sup> We have recently reported the synthesis of the first stable triphospha[3]radialene **1**, where the three exo-carbon atoms of a [3]radialene skeleton are replaced by phosphorus atoms.<sup>2</sup> Compound **1** exhibits unique electronic properties due to the cross- $\pi$ -conjugation including three P=C  $\pi$  bonds. From the viewpoint of further functionalization of the triphospha[3]radialene for pursuit of its application with specific functions, we are interested in the modification of the reactive P=C moieties. Sulfurization reaction of P=C bond compounds bearing bulky 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (Mes<sup>\*</sup>) group and their

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**Figure 1** (a) Sulfurization of 4,5,6-triphospha[3]radialene 1. Mes<sup>\*</sup> = 2,4,6-(t-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>. (b) Molecular structure of **2** with thermal ellipsoids set at 50% probability. Selected bond lengths (Å): (a) P1–C1 = 1.656(3), P2–C2 = 1.651(3), P3–C3 = 1.657(3), C1–C2 = 1.437(4), C1–C3 = 1.437(4), C2–C3 = 1.431(4), P1–S1 = 1.9353(12), P2–S2 = 1.9282(12), P3–S3 = 1.9266(12).

desulfurization reproducing the P=C bond reported so far<sup>3</sup> naturally prompted us to examine the sulfurization of the triphospha [3] radialene as a simple modification of P=C bonds. We report here the sulfurization of 1 to give the corresponding phosphine sulfide together with the structure and properties of the sulfurized product.

#### **RESULT AND DISCUSSION**

The reaction of 1 with elemental sulfur ( $S_8$ , 4.5 eq. as S) in the presence of triethylamine at 80°C for 3 h gave sulfurized compound 2 in 83% as a deep violet solid (Figure 1a). The reaction of 1 with elemental sulfur in the absence of triethyl-amine did not give any sulfurized compound. The three phosphaalkene moieties of compound 1 were converted to methylene(thioxo)phosphorane moieties by the sulfurization reaction. Compound 2 was fully characterized by NMR spectroscopy and elemental analysis, and its structural parameters were definitively determined by X-ray crystallographic analysis (Figure 1b). The central C<sub>3</sub>P<sub>3</sub>S<sub>3</sub> core was revealed to be planar and almost  $C_3$  symmetric. The bond lengths of 2 around the phosphorus atoms are almost the same as those of known methylene(thioxo)phosphorane compounds.

The electronic spectrum of **2** in hexane showed a strong absorption at  $\lambda_{max} = 593$  nm ( $\varepsilon = 3.17 \times 10^4$ ), which is longer than that of **1** at  $\lambda_{max} = 526$  nm ( $\varepsilon = 1.92 \times 10^4$ ) (Figure 2a), indicating the smaller HOMO-LUMO gap of **2** relative to **1**. Cyclic voltammograms of **2** in THF at r.t. exhibited a reversible reduction couple at  $E_{1/2} = -1.38$  V (vs FcH/FcH<sup>+</sup>), showing its higher electron-accepting ability than that of **1** ( $E_{1/2}^{-1} = -1.55$  V vs FcH/FcH<sup>+</sup>) (Figure 2b). The oxidation processes of **1** and **2** under these CV measurement conditions were both irreversible ( $E_{pa} = 1.13$  V for **1**,  $E_{pa} = 0.83$  V for **2**), while the oxidation potential of **2** would be lower than that of **1**.

Desulfurization reaction of 2 with excess amount of tris(dimethylamino)-phosphine (HMPT) in benzene at room temperature for 3 h gave 1 quantitatively. It can be concluded that the electronic structure and properties should be facilely modified by the sulfurization reaction, and the reproduction of the original triphospha[3]radialene would be also easily achieved by the addition of HMPT. That is, sulfurization reaction should be 'reversible' functionalization toward triphospha[3]radialene.



Figure 2 (a) Electronic spectra in hexane of 2 (solid line) and 1 (broken line). (b), (c) Cyclic voltammograms of 2 (solid line) and 1 (broken line) in the reductive region (b) and oxidative region (c). The measurements were carried out in THF solution (0.1 mM) containing  $0.1 \text{ M} (n-\text{Bu})_4\text{NPF}_6$  as a supporting electrolyte with scan rates of 50 mVs<sup>-1</sup> at ambient temperature.

#### **EXPERIMENTAL**

To a mixture of **1** (87 mg, 0.10 mmol) and elemental sulfur (15 mg, 0.45 mmol as S) in benzene (1 mL) was added triethylamine (0.14 mL, 1.0 mmol). After the reaction at 80°C for 3 h, the volatile materials were removed under reduced pressure. Hexane was added to the residue, and then the mixture was filtered through Celite<sup>®</sup>. After removal of the solvent, the obtained residue was purified by column chromatography on silica gel (hexane/CHCl<sub>3</sub> = 5/1) to give compound **2** (80 mg, 83  $\mu$ mol, 83%). **2**: violet crystals, m.p. 202°C (decomp). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.24 (s, 27H), 1.84 (s, 54H), 7.61 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  31.1 (CH<sub>3</sub>, s), 34.3 (CH<sub>3</sub>, s), 35.4 (C, s), 38.9 (C, s), 122.9 (CH, dd,  $J_{PC} = 5$ , 10 Hz), 154.4–154.5 (C, m), 156.0–156.2 (C, m); <sup>31</sup>P NMR (120 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  91.8 (s); Anal. Calcd for C<sub>57</sub>H<sub>87</sub>P<sub>3</sub>S<sub>3</sub>: C, 71.21; H, 9.12%. Found: C, 70.97; H, 9.19%.

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