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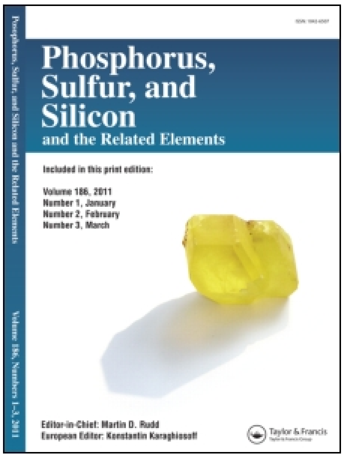

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Formation of Two Novel $^{t}BuNSe(\mu\text{-}N^{t}Bu)_2EO_x$ (E = S, x = 2; E = Se, x = 1) Heterocycles

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Two new chalcogen-nitrogen heterocycles, $^{t}BuNSe(\mu\text{-}N^{t}Bu)_2SO_2$ (1) and $^{t}BuNSe(\mu\text{-}N^{t}Bu)_2SeO$ (2), have been prepared by the reaction between $^{t}BuNH_2$, $SeCl_4$, and SO_2Cl_2 or $SeOCl_2$. $^{t}BuNSe(\mu\text{-}N^{t}Bu)_2SeO$ can also be generated by cycloaddition reaction of tBuNSeNtBu with $^{t}BuNSeO$. Both (1) and (2) contain a slightly puckered four-membered E_2N_2ring, containing nitrogen chalcogen single bonds. The length of the exocyclic nitrogen-selenium bond in both molecules indicates a double bond.

Products have been identified and characterized by using X-ray diffraction, NMR spectroscopy and elemental analysis.

Keywords: Chalcogen-nitrogen-compounds; NMR spectroscopy; crystal structure

INTRODUCTION

Selenium(IV) diimides RN=Se=NR have been known since 1976, but they are thermally unstable.[1,2] The first cyclic selenium imides, $Se_6(N^{t}Bu)_2$ and $Se_9(N^{t}Bu)_6$ have been prepared by Roesky *et al.*[3], and

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we have recently reported the preparation of a $(SeN^tBu)_3$ ring compound containing no Se-Se bonds.[4] In this paper we describe syntheses and characterization of **1** and **2**.

EXPERIMENTAL SECTION

All manipulations involving air-sensitive materials were conducted under an argon atmosphere. Solvents were dried and distilled prior to use. $^tBuNSeN^tBu$ was prepared from $SeCl_4$ and $^tBuNH_2$.[5]

Instrumentation. ^1H NMR spectra were recorded on a Bruker AM-200 spectrometer and ^{13}C, ^{14}N and ^{77}Se spectra were recorded on a Bruker DPX-400 spectrometer. Diffraction data were collected on a Nonius Kappa CCD diffractometer at 173 K by recording 180 frames via φ-rotation (Δφ = 2°; two times 40-60 s per frame).

Preparation of $^tBuNSe(\mu\text{-}N^tBu)_2SO_2$

$^tBuNH_2$ (5.3 ml, 54 mmol) was added to a mixture of $SeCl_4$ (1.325 g, 6.0 mmol) and SO_2Cl_2 (0.810 g, 6.0 mmol) in THF (40 ml) at -80°C. The reaction mixture was stirred for 1.5 h at -80°C and then for 1 h at 23°C. The precipitate of $(^tBuNH_3)Cl$ was separated by filtration and the solvent was removed from the yellow filtrate under vacuum. The solid residue was extracted with *n*-hexane (20 ml) and the hexane solution was cooled to -18°C to give $^tBuNSe(\mu\text{-}N^tBu)_2SO_2$ (0.177 g, 0.33 mmol, 8%). Anal. Calc. For $C_{12}H_{27}N_3O_2SSe$: C, 40.44; H, 7.64; N, 11.79. Found: C, 39.61; H, 7.66; N, 11.75. NMR: δ ^1H (C_7D_8, 25°C) 1.44 (s,NC_4H_9, 9 H), 1.32 (s, μ- NC_4H_9, 18 H); δ ^{13}C (C_7D_8, 25°C) 63.2 [$C(CH_3)$], 59.2 [$C(CH_3)$], 32.1 [$C(CH_3)$], 30.0 [$C(CH_3)$]; δ ^{14}N (C_7D_8, 25°C) –167 and –206; δ ^{77}Se (C_7D_8, 25°C) 824.

Preparation of ${}^tBuNSe(\mu\text{-}N^tBu)_2SeO$

Prepared like 1 except instead of SO_2Cl_2 $SeOCl_2$ (0.995 g 6.0 mmol) was used. Yellow crystals of ${}^tBuNSe(\mu\text{-}N^tBu)_2SeO$ (0.275 g, 0.71 mmol, 12%). Anal. Calc. For $C_{12}H_{27}N_3OSe_2$: C, 37.22; H, 7.03; N, 10.85. Found: C, 36.82; H, 6.98; N, 10.60. NMR: δ ${}^{77}Se$ (*n*-hexane, 25°C) 882, 1175.

RESULTS AND DISCUSSION

${}^tBuNSe(\mu\text{-}N^tBu)_2SO_2$ (1) was identified by ${}^1H$, ${}^{13}C$, ${}^{14}N$ and ${}^{77}Se$ NMR and by X-ray crystallography. The X-ray structure showed a four-membered Se(IV)NSN ring, with long nitrogen-selenium distances of 1.948(2) and 1.958(2) Å (c.f. the Se-N single bond length of 1.85).[6] Terminal Se-N distance is 1.665(2) Å indicating a double bond. 1 can also be formed from the reaction of $({}^tBuNH)_2SO_2$ formed *in situ*[7] and the putative ${}^tBuNSeCl_2$[4].

The structure of ${}^tBuNSe(\mu\text{-}N^tBu)_2SeO$ (2) was shown by X-ray crystallography to involve a puckered four-membered Se(IV)NSe(IV)N ring with the two exocyclic substituents in a *cis* configuration. The terminal $Se{=}N^tBu$ and $Se{=}O$ bond lengths are 1.687(4) and 1.628(4) Å indicating double bonds. The bridging Se-N bond lengths are 1.864 Å in case of the selenium atom attached to oxygen and 1.936 Å in case of that bonded to a terminal N^tBu group. The bridging nitrogen atoms are pyramidal ($\Sigma\!< N(2) = 336.4°$, $\Sigma\!< N(3) = 338.1°$). The decomposition of 2 in toluene gives rise to ${}^tBuNSeO$ (δ 1252 ppm) and ${}^tBuNSeN^tBu$ (δ 1652 ppm), together with $Se_3({}^tBuN)_2$ (1626 and 1183 ppm) and $(SeN^tBu)_3$ (1396 ppm). 2 can be viewed as a [2+2] cycloaddition product of ^{t}BuNSeN^{t}Bu and ^{t}BuNSeO, which both are unstable as monomers.[6] In fact, 2 can be generated from ^{t}BuNSeN^{t}Bu and ^{t}BuNSeO in *n*-hexane. After 2 days equimolar mixture shows the ^{77}Se NMR resonances of **2** (25 %) and ^{t}BuNSeN^{t}Bu (75 %).

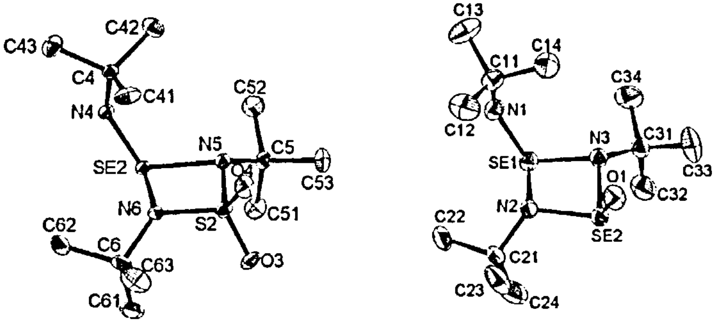

FIGURE 1. Molecular structures of **1** and **2**.

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