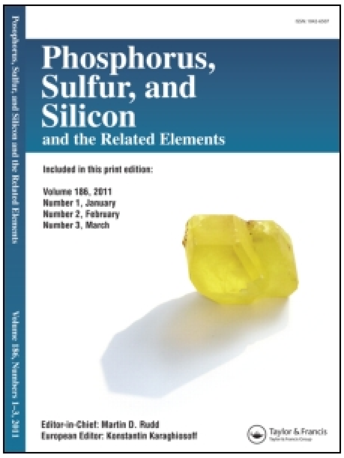

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Synthesis and Characterization of 10-Se-3 Type Selenatetraazapentalene Derivatives with A Hypervalent Selenium

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SYNTHESIS AND CHARACTERIZATION OF 10-Se-3 TYPE SELENATETRAAZAPENTALENE DERIVATIVES WITH A HYPERVALENT SELENIUM

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Abstract Symmetrical 12π-selenatetraazapentalene derivatives 3-5 were synthesized by a convenient one-pot reaction using the lithium selenoureide/phenacyl chloride/alkyl (or allyl) isothiocyanate system. The structure was determined by a single crystal X-ray diffraction of 4. The reactions of 3 and 5 with alkyl iodides and ω-bromoalkyl isothiocyanates gave the novel selenatetraazapentalene derivatives.

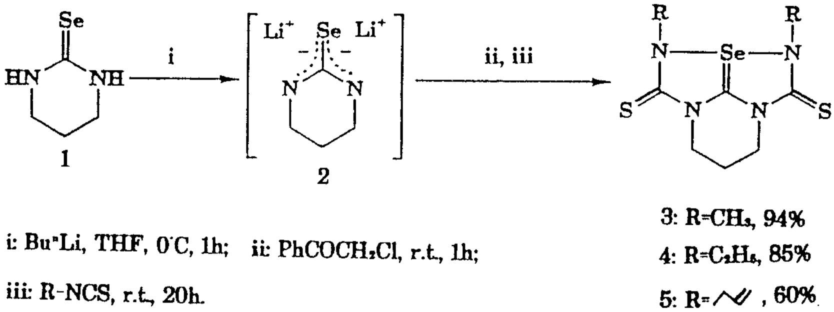
INTRODUCTION

The chemistry of 1,6,6a-trithia(6a-S^{IV})pentalene and analogous compounds has attracted much attention because of their unusual electronic structure, and many 6a-thia(S^{IV})pentalene derivatives containing 10π-electrons in the framework were synthesized.[1-9] Recently, we have reported the synthesis and reactivity of 12π-tetraazapentalene derivatives which have 10-S-3 type structure.[10] In the course of our studies, we have found that the 12π-selenatetraazapentalene derivatives (3-5) containing a hypervalent selenium and two thiocarbonyl groups in framework are synthesized in good yields by a convenient one-pot reaction using the lithium selenoureide/phenacyl chloride/alkyl isothiocyanate system. We now report the synthesis, structure, and chemical behavior of the 12π-selenatetraazapentalene derivatives.

RESULTS AND DISCUSSION

The selenourea (1) was prepared by the reaction of S,S'-dimethyl dithioselenocarbonate[11] with 1,3-propanediamine. The reaction was carried out under argon in tetrahydrofuran (THF) at room temperature for 1 h. Purification with flash-chromatography gave the cyclic selenourea 1 in 35% yield. Compound 1 was slightly unstable and colored gradually to red in air. Compound 1 was treated under argon with two molar equivalents of butyllithium in THF at 0°C for 1 h. The resulting dianion (2) was allowed to react with a molar equivalent of phenacyl chloride at room temperature for 1 h. Then a solution of alkyl isothiocyanates ($R=CH_3$, CH_3CH_2, and $CH_2=CHCH_2$; three times molar quantity of 1) in THF was added and the reaction mixture was stirred at room temperature for 20 h. Usual work-up and purification afforded the selenatetraazapentalene derivatives 3-5 in high yields, as shown in Scheme 1.

Scheme 1



i: Bu^nLi, THF, 0°C, 1h; ii: $PhCOCH_2Cl$, r.t., 1h;
iii: R-NCS, r.t., 20h.

3: $R=CH_3$, 94%
4: $R=C_2H_5$, 85%
5: R= , 60%

Compounds 3-5 were considerably stable in air. UV spectra of 3-5 in acetonitrile solution exhibited a strong absorption band near 260 nm and no absorption band in the visible region. The structure of 1 and 3-5 was determined by IR, ^1H-NMR, ^{13}C-NMR, and mass spectra, and elemental analyses.

Structure of Selenatetraazapentalene Derivatives. In order to establish the structure of the selenatetraazapentalene derivatives, a single crystal X-ray diffraction of 4 was performed. The crystals of 4 were the most suitable among those of 3-5 for an X-ray diffraction. Figure 1 shows the molecular structure of 4. The selected bond lengths and angles are listed in Table 1. Figure 2 shows the molecular structure of 4 viewed along the Se(1)-C(3) bond. The structural characteristic of 4 is as follows. (i) The average distance of the Se-N bond (2.03 Å) is longer than that of the normal Se-N single bond (1.87 Å) by 9%; (ii) The C=S bond lengths, 1.702 and 1.676 Å, are clearly longer than the normal bond length of a C=S double bond (1.61 Å); (iii) The Se(1)-C(3) bond length (1.852 Å) is intermediate between those of the Se-C single bond (1.94 Å) and the Se=C double bond (1.74 Å); (iV) The tetraazapentalene framework can be regarded as a planar molecule, because the deviation of the framework atoms from the plane is only 0.018 Å.

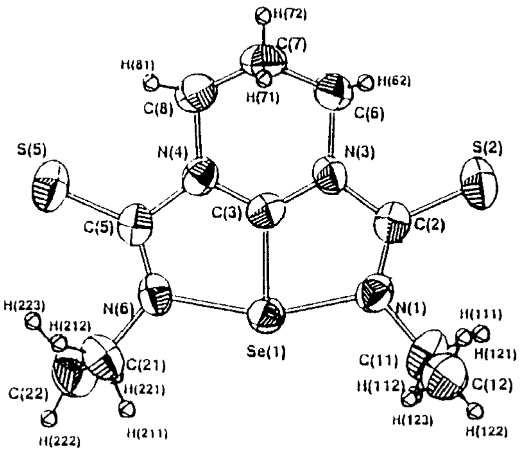


Fig 1. Molecular structure of 4 with numbering scheme

Table 1. Selected Bond Lengths and Angles of 4

Distance/Å		Angle/°	
Se(1)-N(1)	2.022 (6)	N(1)-Se(1)-N(6)	158.5 (2)
Se(1)-N(6)	2.045 (6)	N(1)-Se(1)-C(3)	79.3 (3)
Se(1)-C(3)	1.852 (7)	N(1)-C(2)-N(3)	111.6 (6)
S(2)-C(2)	1.702 (8)	N(1)-C(2)-S(2)	127.9 (6)
S(5)-C(5)	1.676 (12)	N(6)-Se(1)-C(3)	79.2 (3)
N(1)-C(2)	1.293 (9)	N(6)-C(5)-N(4)	109.8 (9)
N(6)-C(5)	1.294 (13)	N(6)-C(5)-S(5)	129.7 (9)
N(3)-C(2)	1.418 (9)	C(2)-N(3)-C(3)	116.0 (6)
N(4)-C(5)	1.445 (13)	C(5)-N(4)-C(3)	117.1 (7)
N(3)-C(3)	1.326 (9)	N(3)-C(3)-N(4)	124.9 (6)
N(4)-C(3)	1.331 (9)		

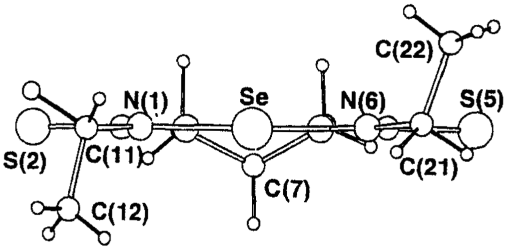
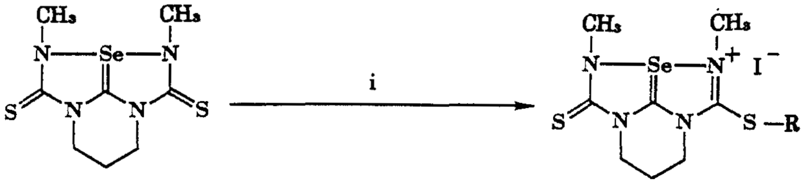


Fig 2. Molecular structure of 4 viewed along the Se(1)-C(3) bond

The Chemical Behavior of Selenatetraazapentalene Derivatives 3-5. (A) The reaction with alkyl iodides: It was found that the selenatetraazapentalene derivative 3 reacts with various alkyl iodides to give regioselectively the S-monoalkylated products (6-8) (Scheme 2).

Scheme 2



3

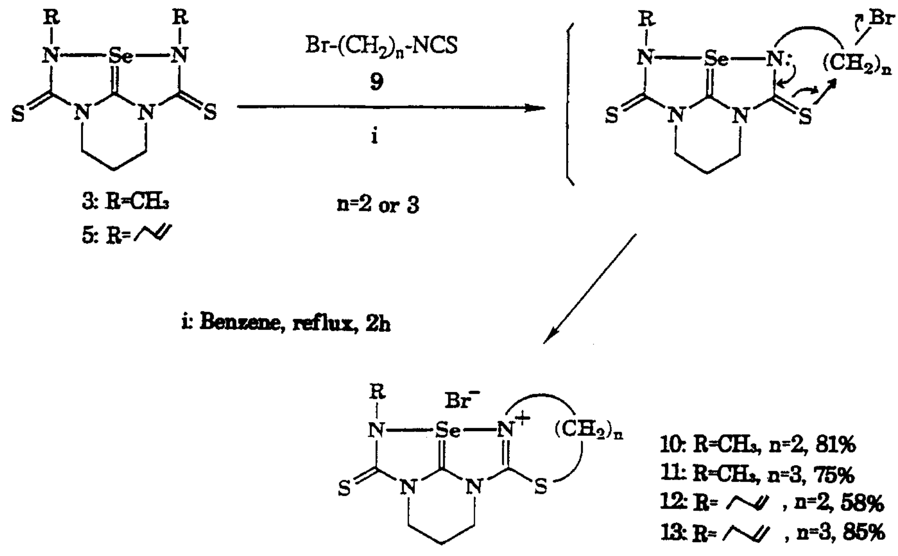
i: R-I, Benzene, reflux, 24h

6: R=CH_3, 83%
7: R=C_2H_5, 86%
8: R=Pr^i, 15%

The selenatetraazapentalene 3 was treated with 100 molar equivalents of alkyl iodides in benzene under reflux for 24 h. The resulting precipitate was filtered off and recrystallized from methanol to give 6, 7, and 8 in the yields shown in Scheme 2. When methyl or ethyl iodide was used, the S-monoalkylated product was obtained in a good yield. However, in the case of isopropyl iodide, the yield became remarkably lower. S-Monoalkylated products were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, UV and mass spectra, and elemental analysis.

(B) The reaction with ω-bromoalkyl isothiocyanates: We have found that the selenatetraazapentalene derivatives 3 and 5 react with ω-bromoalkyl isothiocyanates 9 (n=2 or 3) to give selenatetraazapentalene derivatives (10-13) with fused cyclic system. ω-Bromoalkyl isothiocyanates 9 were prepared from the corresponding ω-bromoalkylamine hydrobromides and thiophosgene according to the method described in the literature.[12] When 3 and 5 were treated in benzene at 80°C for 2 h, a white solid separated out within a few minutes. The resulting colorless precipitate was filtered off, washed with benzene, and recrystallyzed from ethanol to give the selenatetraazapentalenes 10-13 having a fused cyclic system in high yields (Scheme 3).

Scheme 3



The structure of products 10-13 was determined by IR, ^{1}H-NMR and ^{13}C-NMR spectra, and elemental analysis. The IR spectra of 10-13 had no peak in the region of 2000-2200 cm^{-1}. This fact establishes that the structure of 10-13 has not the isothiocyanate group. In general, the products 10-13 were slightly unstable and colored gradually to red in air. Further reactions of 10-13 with ω-bromoalkyl isothiocyanates 9 under similar conditions did not give selenatetraazapentalenes with two fused rings. The S-alkylated selenatetraazapentalenes with the $-S-(CH_2)_n-NCS$ group also were not detected at all. These reactions are considered to proceed by replacement of the isothiocyanate moiety of 3 and 5 by ω-bromoalkyl isothiocyanates, followed by intramolecular cyclization, as shown in Scheme 3.

In conclusion, it was proved that (i) the framework of the 12π-selenatetraazapentalene derivative 4 is planar, (ii) in the alkylation of 3 with alkyl iodides, the external C=S double bond is regioselectively alkylated, (iii) the reactions of 3 and 5 with ω-bromoalkyl isothiocyanates give the novel selenatetraazapentalene derivatives by exchage reaction, followed by intramolecular cyclization, and (iV) selenatetraazapentalenes having a hypervalent selenium are slightly unstable in air.

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