Synthesis of Novel 10-Se-3 Type Selenatetraazapentalene Derivatives with a Hypervalent Selenium

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Synopsis. Novel selenatetraazapentalene derivatives, 2,3-disubstituted 6,7-dihydro-5*H*-2a-selena(*2a*-Se^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione, were synthesized by a convenient one-pot reaction using the lithium selenoureide/phenacyl chloride/alkyl isothiocyanate system in good yields.

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] We have recently reported that 12π-thiatetraazapentalene derivatives having π-hypervalent sulfur and two thiocarbonyl groups in the frameworks are synthesized by a convenient one-pot reaction using the lithium thioureide/phenacyl chloride/alkyl isothiocyanate system.[2] However, compounds of this type have not been so well-investigated to date.[3] For a detailed study of the physical and chemical properties of this 12π-tetraazapentalene derivatives, we have tried a synthesis of 12π-selenatetraazapentalenes having a hypervalent selenium (10-Se-3 type).

In this paper, we report the synthesis of 2,3-disubstituted 6,7-dihydro-5*H*-2a-selena(*2a*-Se^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**4**) and its spectral characterization.

Results and Discussion

The 6-membered-ring selenourea (**2**) was prepared by the reaction of *S*,*S*′-dimethyl dithioselenocarbonate (**1**)[4] with 1,3-propanediamine. The reaction was carried out in tetrahydrofuran (THF) at room temperature for 1 h under argon, and further purification with flash-chromatography afforded cyclic selenourea **2** in 35% yield. Selenourea **2** was slightly unstable and colored to red gradually under the atmosphere.

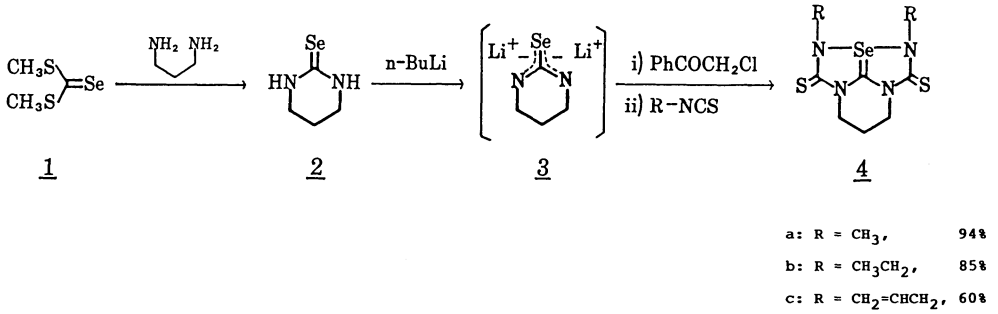
Synthetic reaction of selenatetraazapentalene derivatives **4** was carried out under the same conditions which were used in the synthesis of 10-S-3 type thiatetraazapentalenes.[2] Selenourea **2** was treated with two molar equivalents of butyllithium in THF at 0 °C for 1 h under argon. The resulting dianion (**3**) was allowed to react with a molar equivalent of phenacyl chloride under reflux for 1 h. After cooling to room temperature, a solution of alkyl isothiocyanate (R=CH_3, CH_3CH_2, or CH_2=$CHCH_2$; three times molar quantity of **2**) in THF was added, and the reaction mixture was stirred at room temperature for 20 h. Usual workup and purification gave selenatetraazapentalene derivatives **4a—c** in poor yields (7—12%). It is considered that the poor yields of **4** are due to the thermolability of the dianion **3**. Therefore, the reaction of the dianion **3** with phenacyl chloride was carried out at room temperature. Consequently, the yields of 10-Se-3 type selenatetraazapentalene derivatives **4** have risen remarkably. Scheme 1 shows the reaction pathway for the formation of **4** and the yields of products.

Compounds **4** are considerably stable in air. UV spectra of **4a—c** in acetonitrile show a strong absorption band near 260 nm, and there is no absorption band in the visible region. The structure of **4** was determined by IR, ^{1}H NMR, ^{13}C NMR, mass spectra, and elemental analyses.

Experimental

General. Melting points were determined on a Yanagimoto MP-S3 melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM-GX270 spectrometer. Chemical shifts are reported in ppm from TMS as an internal standard and are given in δ units. The IR and UV spectra were determined on a Hitachi 215 Grating infrared spectrometer and Shimadzu UV-265 spectrometer, respectively. Mass spectra were obtained with a Shimadzu LKB-9000 instrument equipped with a solid injector; the ionizing voltage was 70 eV. Purifications of products were conducted by column chromatography on silica gel (Wakogel C-300).

3,4,5,6-Tetrahydro-2(1*H*)-pyrimidineselenone (2). 1,3-Propanediamine (2.87 mmol) was added dropwise to a solution of *S*,*S*′-dimethyl dithioselenocarbonate (**1**) (1.89 mmol) in 30 ml of tetrahydrofuran (THF) at room temperature



Scheme 1.

under argon. The reaction mixture was stirred under the same conditions for 1 h. After THF was evaporated, the residue was flash-chromatographed on silica gel (chloroform:ethyl acetate=3:1 as an eluent) to give 108 mg of **2** in 35% yield. Reprecipitation from hexane and then recrystallization from methanol afforded pure **2** as a colorless solid: mp 198—201 °C (decomp); IR (KBr) 3180 (NH), 2940, 1560, 1315, and 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.99 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.31 (d of t, 4H, J=2.0 and 6.0 Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$), and 7.06 (br, 2H, NH); MS m/z (rel intensity) 166 (M^++2; 18), 164 (M^+, based on ^{80}Se isotope peak; 100), 162 (M^+−2; 48), 149 (8), 116 (26), 84 (24), and 83 (25). The microanalysis (C, H, N) was in satisfactory agreement with the calculated value within ±0.5%.

Typical Procedure for the Synthesis of 4. To a cooled THF solution (0 °C, 25 ml) of **2** (94 mg, 0.58 mmol) was added a hexane solution of butyllithium (1.25 mmol) with stirring at 0 °C under argon, and the mixture was stirred for 1 h under the same conditions. To the resulting dianion **3** was added dropwise a THF solution (5 ml) of phenacyl chloride (0.58 mmol). After stirring at room temperature for 1 h under argon, a solution of methyl isothiocyanate (1.74 mmol) in THF (5 ml) was added, and the reaction mixture was stirred under the same conditions for 20 h. After THF was evaporatd, the residue was poured into an aqueous ammonium chloride. The solution was extracted with chloroform, and the extract was washed with water, dried over anhydrous Na_2SO_4, and condensed under reduced pressure. Flash-chromatography of the residue on silica gel using chloroform as an eluent gave 167 mg (94%) of **4a** as a colorless solid. Recrystalization from hexane–chloroform afforded a pure sample.

2,3-Dimethyl-6,7-dihydro-5*H*-2a-selena(2*a*-Se^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithoine (4a). Mp 213—216 °C (decomp); IR (KBr) 2930, 1575, 1535, 1500, 1185, and 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.36 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.32 (s, 6H, 2×$CH_3$), and 4.49 (t, 4H, J=6.0 Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$); ^{13}C NMR ($CDCl_3$) δ=20.28, 33.52, 46.48, 159.21, and 171.13; UV (CH_3CN) 213 (log ε 4.23), 259 (4.41), ca. 290 (sh, 3.85), and 325 nm (3.56); MS m/z (rel intensity) 237 (3), 235 (M^+−CH_3NCS, based on ^{80}Se isotope peak; 10), 233 (4), 193 (3), 122 (4), 97 (8), 73 (100), 72 (55), and 69 (29). Found: C, 31.23; H, 4.06; N, 18.33%. Calcd for $C_8H_{12}N_4S_2Se$: C, 31.27; H, 3.94; N, 18.23%.

2,3-Diethyl-6,7-dihydro-5*H*-2a-selena(2*a*-Se^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (4b). Mp 195—198 °C (decomp); IR (KBr) 2960, 2920, 1570, 1535, 1480, 1305, 1180, and 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (t, 6H, J=7.0 Hz, 2×$CH_2C\underline{H}_3$), 2.36 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.87 (q, 4H, J=7.0 Hz, 2×$C\underline{H}_2CH_3$), and 4.50 (t, 4H, J=6.0 Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$); ^{13}C NMR ($CDCl_3$) δ=14.23, 20.23, 42.58, 46.21, 159.41, and 169.91; UV (CH_3CN) 215 (log ε 4.28), 261 (4.48), ca. 292 (sh, 3.90), and 325 nm (3.65); MS m/z (rel intensity) 251 (6), 249 (M^+−CH_3CH_2NCS, based on ^{80}Se isotope peak; 31), 247 (16), 111 (10), 87 (100), 83 (36), and 72 (36). Found: C, 35.76; H, 4.96; N, 16,70%. Calcd for $C_{10}H_{16}N_4S_2Se$: C, 35.82; H, 4.81; N, 16.71%.

2,3-Diallyl-6,7-dihydro-5*H*-2a-selena(2*a*-Se^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (4c). Mp 164—167 °C (decomp); IR (KBr) 2950, 1565, 1515, 1460, 1305, 1160, 1130 and 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.37 (m, 2H, J=6.0 Hz, $NCH_2C\underline{H}_2CH_2N$), 4.44 (m, 4H, 2×$CH_2$=$CHC\underline{H}_2N$), 4.51 (t, 4H, J=6.0 Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$), 5.25—5.34 (m, 4H, 2×$C\underline{H}_2$=$CHCH_2N$), and 5.92—6.07 (m, 2H, 2×CH_2=$C\underline{H}CH_2$-N); ^{13}C NMR ($CDCl_3$) δ=20.19, 46.33, 50.53, 118.79, 132.69, 160.13, and 170.64; UV (CH_3CN) 215 (log ε 4.32), ca. 242 (sh, 4.19), 261 (4.45), ca. 290 (sh, 3.90), and 328 nm (3.67); MS m/z (rel intensity) 263 (7), 261 (M^+−CH_2=$CHCH_2NCS$, based on ^{80}Se isotope peak; 10), 259 (5), 99 (100), 72 (29), and 67 (16). Found: C, 40.46; H, 4.54; N, 15.36%. Calcd for $C_{12}H_{16}N_4S_2Se$: C, 40.11; H, 4.49; N, 15.59%.

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