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NOVEL RING OPENING REACTION OF 2-ARYL-1,2-BENZISOSELENAZOL-3(2H)-ONE WITH THIOLS

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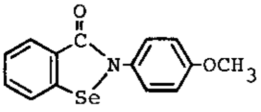
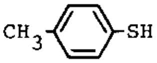
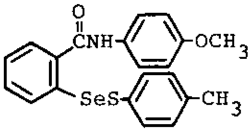
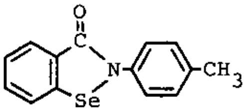
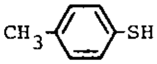
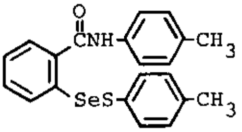
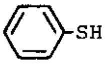
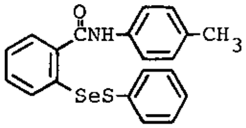
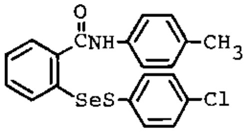
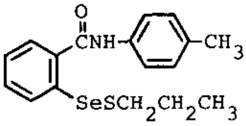
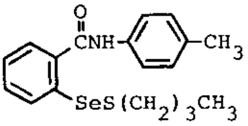
Abstract — Reaction of 2-aryl-1,2-benzisoselenazol-3(2H)-one (1) with alkane- and arenethiols in dichloromethane at room temperature gives ring opening adducts, 2-alkyl- and 2-arylthioselenobenzanilides, respectively, probably via nucleophilic reaction of carbonyl oxygen of compound 1 to thiol hydrogen to give 3-hydroxy-2-aryl-1,2-benzisoselenazolium ion and thiolate anion, and subsequent nucleophilic attack on selenium atom by the resulting thiolate anion to generate the final ring opening product.

Although the chemistry of organoseleniums is growing rapidly,[1] little attention has been paid to the heterocycles involving selenium atom in the ring skeleton. In our systematic investigations of benzisothiazolinones[2] and benzisoselenazolinones[3] including photochemical behavior of these compounds, we found that 2-aryl-1,2-benzisoselenazol-3(2H)-one[4] reacts with thiols to give ring opening adducts in high yields. The results will be described in this communication.

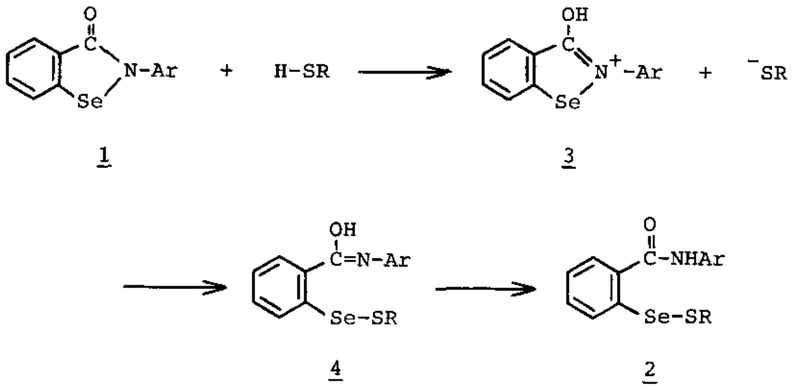
In a typical example, a solution of 152 mg (0.5 mmol) of 2-(4-methoxyphenyl)-1,2-benzisoselenazol-3(2H)-one (1a) and 75 mg (0.6 mmol) of p-toluenethiol in 30 ml of dichloromethane was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give a yellow solid which was purified by preparative TLC on silica gel using benzene as an eluent. The isolated compound (207 mg) was deduced as 2-(p-methylphenylthioseleno)-4'-methoxybenzanilide (2a) on the basis of its spectral data, and consequently the yield was determined to be 97%. Similarly, several reactions of 2-(4-methylphenyl)-1,2-benzisoselenazol-

3(2H)-one (<u>1b</u>) and thiols in dichloromethane were carried out, and the results are summarized in the Table.[5]

Table. Reaction of 2-Aryl-1,2-benzisoselenazol-3(2H)-one with Thiols

Substrate	Thiol	Product	Yield (%)
 (<u>1a</u>)		 (<u>2a</u>)	97
 (<u>1b</u>)		 (<u>2b</u>)	97
<u>1b</u>		 (<u>2c</u>)	95
<u>1b</u>		 (<u>2d</u>)	99
<u>1b</u>	$CH_3CH_2CH_2SH$	 (<u>2e</u>)	96
<u>1b</u>	$CH_3(CH_2)_3SH$	 (<u>2f</u>)	94

The reaction seems to proceed via a nucleophilic attack of the carbonyl oxygen on the hydrogen atom of p-toluenethiol affording 3-hydroxy-2-aryl-1,2-benzisoselenazolium ion (<u>3</u>) and thiolate anion. The anion attacks the selenium atom of the intermediate <u>3</u> and ring opening reaction occurs to give N-(o-alkylthio- or arylthioseleno-α-hydroxybenzylidene)aniline (<u>4</u>) which readily tautomerizes to thioselenobenzanilide (<u>2</u>).



The nucleophilicity of the carbonyl group of compound 1 may be accounted for by the electron donating contribution of lone pair electron of nitrogen. A few related ring opening reactions have been reported previously. Crow and Gosney have reported the ring opening reaction of isothiazolinones by the nucleophilic attack of carbanions on the sulfur atom.[6] Recently, Vernon et al. have assumed that cyanide ion attacks on selenium atom of cyclic ammonium selenide intermediate to give ring opening product in the rearrangement of 1,2-benzselenazoles to 2-(2-pyridyl)phenyl selenocyanate.[7]

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3. N. Kamigata, H. Iizuka, A. Izuoka, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2179.
4. 2-Aryl-1,2-benzisoselenazol-3(2H)-ones were prepared by the methods described previously (see reference 3).

5. The physical and spectral data of the products **2a**-**f** are as follows:

2a: Mp 127-128 °C; IR (KBr) 3300 and 1630 cm^{-1}; ^{1}NMR (DMSO-d_6) $\delta = 2.23$ (3H, s), 3.72 (3H, s), 6.84 (2H, d, $J = 8.4$ Hz), 6.97 (2H, d, $J = 7.8$ Hz), 7.29 (2H, d, $J = 7.8$ Hz), 7.56 (2H, d, $J = 8.4$ Hz), and 10.32 (1H, s); MS, m/z 429 (M$^+$, ^{80}Se) and 305; HRMS, m/z 429.0301 ($C_{21}H_{19}NO_2S^{80}Se$ requires 429.0301).

2b: Mp 207-208 °C; IR (KBr) 3300 and 1620 cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 2.30$ (3H, s), 3.14 (3H, s), 6.9-8.2 (12H, m), and 10.32 (1H, s); MS, m/z 413 (M$^+$, ^{80}Se) and 290; HRMS, m/z 413.0348 ($C_{21}H_{19}NOS^{80}Se$ requires 413.0352).

2c: Mp 162-163 °C; IR (KBr) 3300 and 1630 cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 2.29$ (3H, s), 7.1-8.1 (13H, m), and 10.32 (1H, s); MS, m/z 399 (M$^+$, ^{80}Se) and 290; HRMS, m/z 399.0913 ($C_{20}H_{17}NOS^{80}Se$ requires 399.0195).

2d: Mp 218-219 °C; IR (KBr) 3300 and 1630 cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 2.31$ (3H, s), 7.13 (2H, d, $J = 9.0$ Hz), 7.45 (2H, d, $J = 9.0$ Hz), 7.2-8.3 (8H, m), and 10.30 (1H, s); MS, m/z 433 (M$^+$, ^{35}Cl and ^{80}Se) and 290; HRMS, m/z 433.0581 ($C_{20}H_{16}NO^{35}ClS^{80}Se$ requires 433.0590).

2e: Mp 103-104 °C; IR (KBr) 3300 and 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.87$ (3H, t, $J = 6.6$ Hz), 1.2-1.6 (2H, m), 2.29 (3H, s), 2.78 (2H, t, $J = 6.6$ Hz), 7.14 (2H, d, $J = 9.0$ Hz), 7.45 (2H, d, $J = 9.0$ Hz), 7.2-8.2 (4H, m), and 10.34 (1H, s); MS, m/z 365 (M$^+$, ^{80}Se) and 290; HRMS, m/z 365.0345 ($C_{17}H_{19}NOS^{80}Se$ requires 365.0352).

2f: Mp 97-98 °C; IR (KBr) 3300 and 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.86$ (3H, t, $J = 6.6$ Hz), 1.1-1.8 (4H, m), 2.28 (3H, s), 2.77 (2H, t, $J = 6.6$ Hz), 7.15 (2H, d, $J = 9.0$ Hz), 7.46 (2H, d, $J = 9.0$ Hz), 7.2-8.3 (4H, m), 10.35 (1H, s); MS, m/z 379 (M$^+$, ^{80}Se) and 290; HRMS, m/z 379.0510 ($C_{18}H_{21}NOS^{80}Se$ requires 379.0508).

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