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STABILISATION OF CONDENSED SELENIUM HETEROCYCLES BY A NITRO GROUP IN THE *ORTHO*-POSITION TO THE CHALCOGEN.

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Key Words : glutathione peroxidase; selenenamide; benzisoselenazolinone; 2,1-benzoxaselenol-3-one; 2,1-benzothiaselenol-3-one.

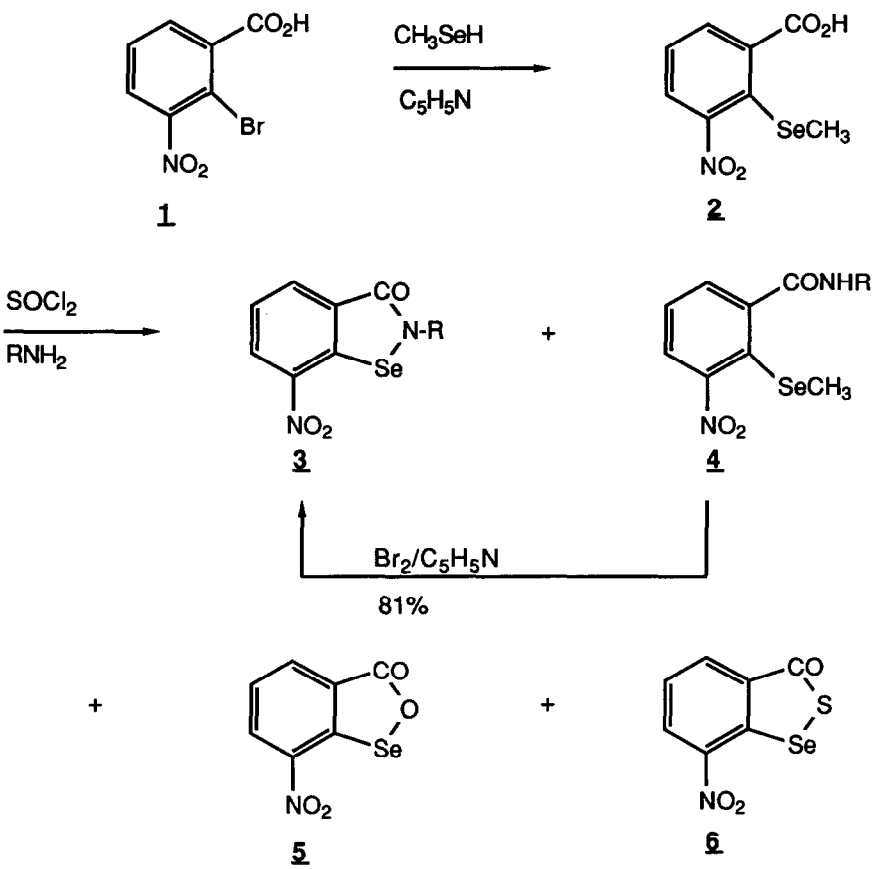
Abstract : The synthesis of the 7-nitro-2-phenyl-1,2-benzisoselenazol-3(2H)-one 3a leads to an abnormal behavior due to a dipole stabilisation between the nitro group and the selenium atom. The first ever synthesis of a 2,1-benzoxaselenol-3-one 5 is described. The unexpected insertion of a sulfur atom from thionyl chloride results in the formation of the 7-nitro-2,1-benzothiaselenol-3-one 6.

INTRODUCTION.

In 1973, Flohé [2a] and Rotruck [2b] identified selenium as an intrinsic component of some enzymes. The mammalian glutathione peroxidase catalyses the reduction of hydroperoxides by glutathione. Its active site contains a selenocysteine residue and a catalytic mechanism highlighting the pivotal role of the various oxidation states of selenium has been proposed.[3] A model for the bonding of the glutathione to the selenocysteine, as a selenosulfide (thiolselenenate), has also been published.[4] Models suggest that the enzyme exists in its oxidised form as a cyclic selenenamide which can be readily reduced to the selenosulfide by thiols.[5]

These kinds of cyclic selenenamides exist in the 1,2-benzisoselenazolin-3-ones described initially by Lesser and Weiss [6] in and later by other groups.[7] It has been demonstrated that their selenium center readily undergoes nucleophilic attack by thiols, yielding an acyclic selenosulfide.[8] Pharmacological studies have shown that the 2-phenyl-1,2-benzisoselenazolinone has interesting antiinflammatory and glutathione peroxidase-like activities in animal models.[9,10] More recently, its principal metabolites have been characterised and synthesised [11,12] and a mechanism for the catalytic reduction of hydroperoxides has been proposed.[13]

It has been shown that a nitro-group can stabilise a selenium functionality in the *ortho*-position by an oxygen-selenium dipole interaction. The *o*-nitrobenzeneselenenyl sulfides form a loose five-membered ring with the selenium, one oxygen, the nitrogen and two carbon atoms of the benzene ring.[14] Other examples are the *o*-selenenic anhydride, selenenic acid [15], selenenate esters [16], selenenyl bromide [17] and peroxyseleninic acid.[18] *O*-nitrosubstitution also causes a million-fold decrease in the rate of nucleophilic attack on selenenyl halides.[19]



a : R=C_6H_5; b : R=$C_6H_5CH_2$; c : *t*-C_4H_9

SCHEME 1

TABLE 1 Yields of the 7-nitro-1,2-benzisoselenazolin-3(2H)-ones **3**.

	3	**4**	**5**	**6**
C_6H_5	78%	-	-	-
$C_6H_5CH_2$	17%	24%	8%	8%
t-C_4H_9	40%	-	4%	20%

These considerations prompted us to design a synthesis of the 7-nitro-1,2-benzisoselenazolinones 3 in which the nitro-group *ortho* to selenium should interfere with the formation and stability of the intermediates responsible of the glutathione peroxidase-like activity.

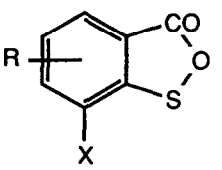
RESULTS AND DISCUSSION.

The 2-methylseleno-3-nitrobenzoic acid 2 was prepared in good yield *via* aromatic nucleophilic substitution of the 2-bromo-3-nitrobenzoic acid 1 [20] by methaneselenol in presence of triethylamine. Treatment of the acid 2 with thionyl chloride, in the presence of a catalytic amount of DMF, followed by aniline afforded the expected benzisoselenazolinone 3a in 78% yield. However, when *tert*-butylamine and benzylamine were used, low yields of 3 were obtained beside other products, the benzamide 4, the 7-nitro-2,1-benzoxaselenol-3-one 5 and the 7-nitro-2,1-benzothiaselenol-3-one 6 (scheme I and table I). 4 could however be cyclised in high yield to the benzisoselenazolinone 3b by reaction with bromine in presence of pyridine.[21]

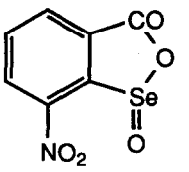
The heterocyclic system 5 was unknown so far. The same CO-O-Se atomic arrangement on two *ortho*-positions of an aromatic ring has been reported [22] but these compounds were Se^{IV}-selenuranes whose Se-O bonds are relatively long compared to 5. Our system is fundamentally different. However, the corresponding sulfenic anhydrides 7 are already known and their structure has been unambiguously established.[23]

We have deduced the structure of 5 on the basis of the following data: Electron impact mass spectrometry produced the parent ion (M^+) at m/z=245, based on ^{80}Se, the isotope pattern identifying one selenium atom present per molecule, with an important degradation peak at m/z=201 (M^+-CO_2). In the IR spectrum, the carbonyl frequency at 1716 cm^{-1} is consistent with a CO-O- atomic arrangement and is close to the ν_{CO}=1752 cm^{-1} of 7a whose higher wavenumber is the result of the transmission of the higher electronegativity of sulfur compared to selenium. The ^1H NMR only shows aromatic protons in an integration ratio of 1:1:1. Apart from the carbonyl resonance at 168.2 ppm, only six aromatic carbons were observed in the ^{13}C NMR spectrum. The very deshielded ^{77}Se NMR signal at 1401 ppm was compared with the signals from related species (for example, the *o*-nitrobenzeneselenenic acid and its anhydride have ^{77}Se chemical shifts of 1066 and 1095 ppm respectively [24]), the deshielding being indicative of the presence of the electron withdrawing carbonyl group on the selenenyl functionality. The structure 5 was unambiguously confirmed by X-ray diffraction analysis. [25]

The 7-nitro-2,1-benzothiaselenol-3-one 6 structure was assigned on the following basis. In the EI mass spectrum, the molecular ion at m/z=261 exhibits the isotope pattern of one selenium atom per molecule and is only 16 a.m.u. higher than the mass of 5, thus corresponding to the selenoxide 8 or to 6 in which an oxygen atom has been replaced by a sulfur. The selenoxide structure could, however, be easily discarded because the selenoxide 8 has been synthesised by oxidation of 5 with hydrogen peroxide and its analytical data are different and, also because an elemental analysis has confirmed that 6 contains one atom of sulfur per molecule. With a ν_{CO} at 1660 cm^{-1}, the IR spectrum indicates that the oxygen replaced by sulfur is the endocyclic one. This value is also really close from the 1630 cm^{-1} of the only analogue of 6 described so far, the unsubstituted 2,1-benzothiaselenol-3-one 9.[6] With only aromatic protons, the ^1H NMR was of little diagnostic use. The ^{13}C NMR has a very deshielded C=O signal at 192.9 ppm as reported for thiolesters and thioanhydrides.[26,27] The ^{77}Se NMR signal at 601.4 ppm was much more shielded that in 5 (1401 ppm) but could usefully be compared with the chemical shift of 9 (542.1 ppm), the difference of 59.3 ppm being easily explained by the deshielding



7 : R=H, *t*-C_4H_9
a : X=NO_2
b : X=CO_2H, CO_2CH_3



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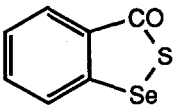

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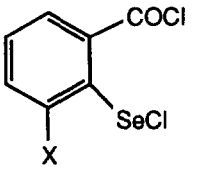
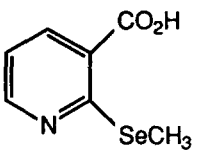


10 : X=H
11 : X=NO_2



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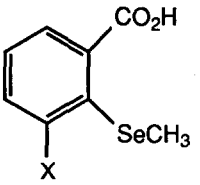

13 a : X=H
b : X=OCH_3
c : X=CO_2H

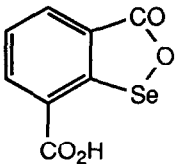

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TABLE 2 Reaction of 2 with various chlorinating agents.

Entry	Chlorinating agent	2 : reagent ratio	5	6
1	$SOCl_2$	1 : 10	40%	40%
2	$SOCl_2$	1 : 2	55%	2%
3	$SeOCl_2$	1 : 10	89%	-
4	$SeOCl_2$	1 : 2	65%	-
5	PCl_5	1 : 1	60%	-
6	Cl_2CHOCH_3	1 : 2	20%	-

effect produced by a nitro group *ortho* to a selenenyl functionality (usually 35 to 120 ppms).[28,29] Finally the structure was definitively confirmed by X-ray diffraction analysis.[30]

The formation of 5 and 6 was further investigated. The acid 2 was reacted with several chlorinating agents in the absence of amine (table 2). We observed that reagents such as phosphorus pentachloride, known to easily chlorodemethylate methylselenoarylethers, were giving good yields of 5. Conversely, the poor Se-chlorodemethylating agent α,α-dichloromethylmethyl ether yielded only 20% of 5 after 24 hrs at reflux in dichloromethane, whereas it was giving 90% yield of amide 4 if the mixture was treated with an amine. It is worthy of note that we were unable to isolate the acid chloride 11 while its unsubstituted analogue 10 is easily accessible.This suggests that the formation of 5 goes through the following steps :1) Chlorodemethylation of the selenoether, 2) Fast cyclisation *via* dehydrochlorination of the selenenyl chloride.

Benzylamine directly reacts with 5 and 6 to give the benzisoselenazolinone 3b in 74 and 20% yield respectively. In the same conditions, the less nucleophilic aniline failed to react. However, it was possible to convert 5 to 3a by treating 5 with thionyl chloride and aniline successively, implying that a more reactive transient bis-electrophile is formed with thionyl chloride.

In a further step, we investigated the reactivity of several *o*-methylselenobenzoic acids toward bromine, an exclusive Se-demethylating agent, in presence of pyridine. Under these conditions, 2 yielded 5 in 75% yield. The 2-methylselenonicotinic acid 12 [21], whose pyridinic nitrogen exhibits -I and -E effects similar to the nitro group, failed to cyclise. In the same manner, the acids 13a and 13b did not yield any cyclic species but only the corresponding diselenides. The 2-methylselenoisophtalic acid 13c was the only one to give the expected five-membered ring 14 in a low but welcome yield of 52% [31], thus demonstrating the necessity of a dipole stabilisation for the formation of the new benzoxaselenolone ring system.

EXPERIMENTAL SECTION.

The proton NMR spectra were recorded on a Bruker WP 200 SY in deutero-chloroform unless otherwise stated. The ^{13}C and ^{77}Se NMR spectra were recorded on a Bruker AM400. All are expressed in δ (ppm). Dimethylselenide was used as external reference for the ^{77}Se NMR. The low-resolution mass spectra were determined at 70 eV on a Varian MAT 112; the presence of a correct isotope pattern for selenium is indicated between brackets. Infrared spectra were recorded on a Perkin Elmer 599 apparatus in KBr pellets. The elemental analyses were obtained on a Hewlett-Packard 185 B. Merck Kieselgel 60 (70-230 mesh) was used for the chromatography. The solvents were dried by standard methods.[32]

2-Methylseleno-3-nitrobenzoic acid 2.

A solution of methaneselenol (9.5 g, 5.9 ml, 0.1 mole) in pyridine (30 ml) was added slowly to a solution of 2-bromo-3-nitrobenzoic acid 1 (24.6 g, 0.1 mole) in pyridine (125 ml) and triethylamine (15 ml) at 0°C. After stirring for 4 hrs at 25°C, the reaction mixture was poured on a mixture of ice and hydrochloric acid. The precipitate was filtered and recrystallised from toluene (mp: 138-142°C). Yield: 20.6g, 79%.
^1H NMR (CD_3OD) : 2.15 (s, 3H, $SeCH_3$, $J_{^{77}Se-H}$=12 Hz); 6.6-7.15 (m, 3H, $H_{arom.}$). ^{13}C NMR : 10.3 ($SeCH_3$, $J_{^{77}Se-^{13}C}$=64.7 Hz); 125.6; 126.0; 127.3 (C2, C4, C5); 132.6 (C6); 139 (C1); 153.9 (C3); 168.0

(COOH). IR: ν_{CO}=1710 cm^{-1}. MS: M^+=261 (^{80}Se). $C_8H_7NO_4Se$ requires C, 36.94; H, 2.71; N, 5.38; O, 24.60; Se, 30.36. Found: C, 36.66; H, 2.89; N, 5.28; O, 24.43; Se, 30.20.

Benzisoselenazolin-3-ones 3a and 3c.

The acid 2 (3.6 g, 0.014 mole) and a catalytic amount of DMF were heated for 4 hrs at reflux in neat thionyl chloride (20 ml). The excess of thionyl chloride was removed under reduced pressure and the residue redissolved in dichloromethane (50 ml). The amine (0.03 mole) in dichloromethane (10 ml) was added dropwise. The resulting solution was stirred overnight, then washed successively with 2 M hydrochloric acid (100 ml) and 10% sodium hydrogen carbonate solutions (100 ml). The organic layer was dried on magnesium sulfate and the solvent was evaporated under reduced pressure.

3a: The residual solid was recrystallised from toluene (mp: 160-163°C). Yield: 3.5 g, 78%.

^1H NMR : 7-8 (m, 6H, $H_{arom.}$); 8.28 (dd, J=8 Hz and not measurable, 1H, $H_{arom.}$); 8.38 (dd, J=8 Hz and not measurable, 1H, $H_{arom.}$). ^{77}Se NMR : 951. IR: ν_{CO}=1650 cm^{-1}. MS: M^+=320 (^{80}Se). $C_{13}H_8N_2O_3Se$ requires C, 48.92; H, 2.53; N, 8.78; O, 15.04; Se, 24.74. Found: C, 48.83; H, 2.61; N, 8.81.

3c: The residual solid was purified by chromatography on silica. Elution with carbon tetrachloride gave 6 (20%), then with toluene gave 5 (4%) and finally with toluene/methanol - 95/5 gave 3c (40%).

Characteristics of 3c; mp: 145-147°C (from toluene). ^1H NMR : 1.72 (s, 9H, *t*-but); 7.67 (dd, J=10 Hz and 10 Hz, 1$H_{arom.}$); 8.35 (dd, J=10 Hz and not measurable, 1$H_{arom.}$); 8.52 (dd, J=10 Hz and not measurable, 1$H_{arom.}$). IR: ν_{CO}=1650 cm^{-1}. MS: M^+=300 (^{80}Se). $C_{11}H_{12}N_2O_3Se$ requires C, 44.16; H, 4.04; N, 9.36; O, 16.04; Se, 26.39. Found: C, 43.77; H, 4.08; N, 9.03; O, 15,73; Se, 26.75.

2-Benzyl-7-nitro-1,2-benzisoselenazolin-3-one 3b.

A solution of 5 (0.2 g, 0.001 mole) and benzylamine (0.32 g, 0.003 mole) in ethanol (15 ml) was stirred at room temperature for 12 hrs. After removal of the solvent under reduced pressure, the residue was purified by preparative thin layer chromatography using toluene/ethyl acetate - 80/20 as eluent. The product was recrystallised from toluene (mp: 112-115°C). Yield: 0.245 g, 74%.

^1H NMR : 5.05 (s, 2H, CH_2); 7.4 (s, 5H, $H_{arom.}$); 7.96 (dd, J=10 Hz and 10 Hz, 1$H_{arom.}$); 8.45 (dd, J=10 Hz and not measurable, 1$H_{arom.}$); 8.52 (dd, J=10 Hz and not measurable, 1$H_{arom.}$). IR: ν_{CO}=1660 cm^{-1}. MS: M^+=334 (^{80}Se). $C_{14}H_{10}N_2O_3Se$ requires C, 50.47; H, 3.03; N, 8.41; O, 14.40; Se, 23.70. Found: C, 50.10; H, 2.81; N, 8.38; O, 14.15; Se, 23.70.

7-Nitro-2,1-benzoxaselenol-3-one 5.

To a solution of acid 2 (2.6 g, 0.01 mole) and pyridine (1.58 g, 1.6 ml, 0.02 mole) in dichloromethane (50 ml) was slowly added a solution of bromine (1.6 g, 0.5 ml, 0.01 mole) in dichloromethane (10 ml). The solution was stirred at room temperature for 1 hr and then washed with 1M hydrochloric acid (100 ml). The organic layer was dried on magnesium sulfate and evaporated under reduced pressure. The residual solid was crystallised from toluene (mp: 170°C). Yield: 1.8 g, 75%.

^1H NMR : 7.83 (t, J=13 Hz, H_5); 8.5 (d, J=13 Hz) and 8.63 (d, J=13 Hz) (H_4 and H_6). ^{13}C NMR : 124.9 (C_{7a}); 128.4 and 129.1 (C_5 and C_6); 136.3 (C_4); 141.2 (C_{3a}); 145.5 (C_7); 168.2 (C_3). ^{77}Se NMR : 1401. IR: ν_{CO}=1716 cm^{-1}. MS: m/z=245 (M^+, 47%, ^{80}Se); 201 (M^+-CO_2, 34%, ^{80}Se); 175 (M^+-Se, 6%); 143 (32%,

^{80}Se); 117 (36%, ^{80}Se); 75 (100%). $C_7H_3NO_4Se$ requires C, 34.45; H, 1.24; N, 5.74; O, 26.22; Se, 32.35. Found: C, 34.67; H, 1.60; N, 5.50; O, 25.90; Se, 31.90.

7-Nitro-2,1-benzothiaselenol-3-one 6.

A solution of 5 (0.24 g, 0.001 mole) in thionyl chloride (5 ml) was heated at reflux for 4 hrs in presence of a catalytic amount of DMF. The excess of thionyl chloride was evaporated under reduced pressure and the residual solid was purified by chromotography on silica using carbon tetrachloride as eluent. Mp: 144-145°C (toluene). Yield: 0.24 g, 92%.

^{1}H NMR : 7.75 (t, J=12 Hz, H_5); 8.35 (dd, J=12 Hz and not measurable); 8.7 (dd, J=12 Hz and not measurable). ^{13}C NMR : 127.6 and 129.8 (C_5 and C_6); 135.0 (C_{7a}); 135.3 (C_4); 140.9 (C_{3a}); 144.8 (C_7); 192.9 (C_3). ^{77}Se NMR : 601.4. IR: ν_{CO}=1660 cm^{-1}. MS: m/z=261 (M^+, 95%, ^{80}Se); 181 (M^+-Se, 5%); 75 (100%). $C_7H_3NO_3SSe$ requires C, 32.32; H, 1.16; N, 5.38; O, 18.45; S, 12.33; Se, 30.35. Found: C, 32.22; H, 1.37; N, 5.86; S, 12.29.

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