Acta Chemica Scandinavica B 37 (1983) 585–588

Synthesis of the Heteroaromatic Selenatriazole Ring System. 5-Amino-1,2,3,4-selenatriazoles

MOGENS JACOBSEN, LARS HENRIKSEN and ARNE HOLM *

Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

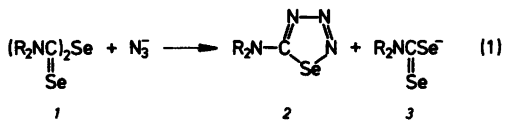
The synthesis of 5-amino-1,2,3,4-selenatriazoles, derivatives of the hitherto unknown selenatriazole ring system, is described. Reaction between bis(*N,N*-disubstituted selenocarbamoyl)selenides and azide ion gives the title compounds in good yield. The reactions of 4,4-dialkylselenosemicarbazides with nitrous acid or an aza-transfer reagent also lead to aminoselenatriazoles. Disubstitued aminoselenatriazoles are thermally unstable decomposing with formation of disubstituted cyanamides, nitrogen and selenium. 5-(Diethylamino)selenatriazole (half-life *ca.* 180 h in $CHCl_3$ at 20 °C) is thermally more stable than 5-(methylphenylamino)selenatriazole. 5-(Alkylamino)selenatriazoles decompose to hydrazoic acid and an isoselenocyanate, and evidence for their formation was only obtained indirectly.

5-Substituted 1,2,3,4-selenatriazoles are hitherto unknown. A report in the literature indicates that they may be highly unstable.[1] Thus stable salts of 1,2,3,4-thiatriazole-5-thiol are formed by reaction of inorganic azides with carbon disulfide while it is found that carbon diselenide reacts with sodium azide in aqueous or aqueous–alcoholic solution with immediate precipitation of red selenium even at −20 °C. It was concluded that *if* a selenatriazole is formed in this reaction it must be extremely unstable.

Introduction of an amino group in the 5-position of the thiatriazole ring causes a significant stabilization decreasing the rate of thermal decomposition leading to nitrogen, sulfur and an organic fragment.[1,2] A similar approach toward the selenatriazole system thus appeared promising. We now report that certain 5-amino-1,2,3,4-selenatriazoles actually can be prepared although they are thermally less stable than the sulfur analogues.

The formation of *N,N*-disubstituted 5-amino-1,2,3,4-selenatriazoles has been investigated by three different reactions. *a.* Reaction between bis(*N,N*-disubstituted selenocarbamoyl)selenides [3] (*1*) and azide ion. *b.* Reaction between 4,4-dialkylselenosemicarbazides and an aza-transfer reagent. *c.* Direct nitrosation of 4,4-dialkylselenosemicarbazide.

Path *a.* The reaction between ammonium azide and bis(*N,N*-diethylselenocarbamoyl)selenide (*1*, R=Et) in methanol proceeds smoothly at room temperature within 24 h according to eqn. 1.

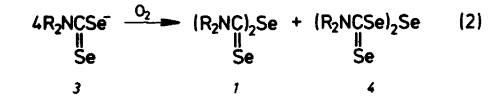


(1)

The diselenocarbamate (*3*) undergoes a facile oxidation by air to give monoselenide *1* and bis(*N,N*-diethyl diselenocarbamato)selenium-(II) [3] (*4*) (eqn. 2). The monoselenide reacts to give additional selenatriazole (*2*) while the triselenide *4* is inactive towards azide ion. Thus 2/3 of the selenocarbamoyl units of *1* may theoretically be converted into *2*. Essentially pure 5-diethylamino-1,2,3,4-selenatriazole has been obtained in 85 % of the theoretical yield.

* To whom correspondence should be addressed.

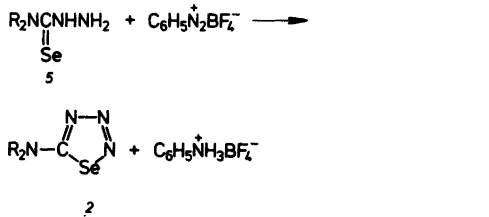
0302-4369/83 $02.50



(2)

5-(Methylphenylamino)-1,2,3-selenatriazole was prepared in the same manner but it is apparently less thermally stable and was isolated in mixture with its decomposition product, methylphenylcyanamide (ratio 1:3).

Path *b*. The aza-transfer reaction, with benzenediazonium tetrafluoroborate or diazotized sulfanilic acid, has recently been investigated with thiosemicarbazides and found to be an alternative method for the preparation of 5-amino-1,2,3,4-thiatriazoles.[4] In the present investigation the reaction between benzenediazonium tetrafluoroborate and 4,4-diethylselenosemicarbazide (*5*) was investigated (eqn. 3) and found to give *2* in a slightly lower yield (70 %) and in less pure state than obtained *via* path *a*.

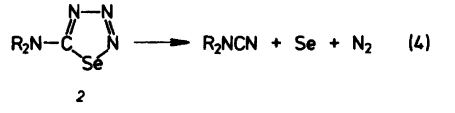


(3)

MS showed the presence of diphenyldiselenide and triselenide as well. The process by which the diphenyl selenides is formed has not been investigated.

Direct nitrosation (path *c*) of 4,4-diethylselenosemicarbazide proceeds with immediate evolution of gases indicating undesired side-reactions and *2* was formed in a low yield (20–30 %) as calculated from ^{1}H NMR spectra.

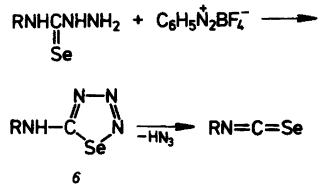
5-Diethylamino-1,2,3,4-selenatriazole is an oil decomposing slowly at room temperature with formation of diethylcyanamide and elemental selenium (eqn. 4). An approximate half-life of 8 days in chloroform at room temperature has been estimated.



(4)

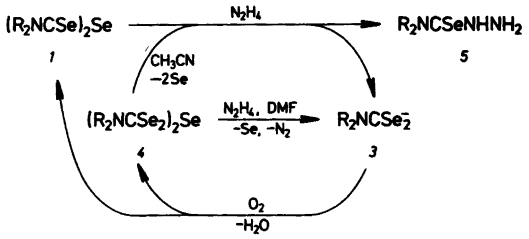
Compound *2* (R=Et) is sufficiently stable to be purified by means of column chromatography but an elemental analysis could not be performed because of its explosive decomposition when heated in oxygen. The structure assignment of *2* is in agreement with MS, ^{1}H NMR and IR analysis (experimental section). The thermal decomposition is similar to that of aminothiatriazoles which gives rise to cyanamides, sulfur and nitrogen although thiatriazoles decompose at a lower rate.[2,3]

The formation of *N*-monosubstituted 5-amino-1,2,3,4-selenatriazoles was investigated by the reaction between 4-benzyl- and 4-cyclohexylselenosemicarbazides and benzenediazonium tetrafluoroborate in methanol (path *b*). With 4-cyclohexylselenosemicarbazide at 0 °C immediate gas evolution and formation of red selenium was observed. An oil was isolated from the reaction mixture which according to GLC/MS consists of a mixture of cyclohexylisoselenocyanate and diphenylselenide. This result indicates formation of 5-cyclohexylamino-1,2,3,4-selenatriazole (*6*, R=cyclohexyl) decomposing with formation of hydrazoic acid and isoselenocyanate (eqn. 5) although attempts to isolate the selenatriazole or observe it by means of ^{1}H NMR were unsuccessful. Monosubstituted 5-aminothiatriazoles undergo a similar decomposition in the presence of base with formation of azide ion and an isothiocyanate.[1] 4-Benzylselenosemicarbazide reacted with benzenediazonium tetrafluoroborate to give a mixture of products among which benzylisoselenocyanate was shown to be present. Again attempts to isolate the selenatriazole were unsuccessful.



(5)

The 4,4-disubstituted selenosemicarbazides were prepared from bis(*N,N*-disubstituted selenocarbamoyl)selenides, *1* [3] and hydrazine in the presence of air. Both selenocarbamoyl moieties of *1* may be utilized when an excess of hydrazine is employed. Thus yields up to 1.4 mol of *5* per mol of *1* have been realized. The reaction is rather complex and can involve two independent reaction cycles as outlined in Scheme 1.



Scheme 1.

The initial step appears to be a nucleophilic substitution on *1* giving one mol of *5* and one mol of diselenocarbamate ion *3*. The subsequent air oxidation of *3* to give a 1:1 mixture of *1* and bis-(*N,N*-dialkyldiselenocarbamato)selenium(II) (*4*) is well documented (see Ref. 3 and refs. cited). The two routes from *4* to *3* were demonstrated when *4* in the absence of oxygen was treated with hydrazine. In DMF as solvent rapid evolution of nitrogen was noted and 1 mmol of *4* (R=Et) yielded 1 mmol of Se together with *3* which was trapped as the *Se*-benzyl ester ($Et_2N-CSe_2-CH_2Ph$, 1.64 mmol). When the same reaction was performed in acetonitrile 2 mmol of Se was produced and evaporation of solvent from the filtrate left a yellow solid which according to ^1H NMR and elemental analysis was a 1:1 mixture of *5* and the hydrazinium salt of *3*. The theoretical stoichiometries of the two reactions are given as eqns. 6 and 7, respectively.

$$4(R_2NCSe)_2Se+10N_2H_4+4O_2 \xrightarrow{DMF} 8R_2NCSeNHNH_2+4Se+2N_2+8H_2O \quad (6)$$

$$4(R_2NCSe)_2Se+8N_2H_4+2O_2 \xrightarrow{CH_3CN} 8R_2NCSeNHNH_2+4Se+4H_2O \quad (7)$$

This solvent dependence may be explained in terms of the structure of *4* which is intermediary between a coordination compound of selenium(II) and a covalent triselenide.[6] Thus, in the better solvating medium, DMF, *4* behaves like a selenium(II) species and oxidizes hydrazine while in the poorer solvating acetonitrile the covalent character of *4* predominates and it undergoes nucleophilic substitution in analogy with *1*.

EXPERIMENTAL

^1H NMR spectra were obtained with a Varian T-60A instrument ($CDCl_3$ and CCl_4; $SiMe_4$ as internal standard). IR spectra were obtained with a Perkin-Elmer 157P infrared spectrophotometer and UV spectra on a Unicam SP 1800 instrument. GLC-MS were obtained with a VG Micromass 7070 instrument operated at 70 eV with an ion source temperature at 220 °C in combination with a 5 % OV 101 column.

4-Monosubstituted selenosemicarbazides were prepared according to known methods.[5]

Preparation of 4,4-diethyl selenosemicarbazide. Monoselenide *1* (1 mmol) was dissolved in acetonitrile (100 ml) hydrazine hydrate (3 mmol) added and the mixture left with stirring for 24 h. The mixture was filtered through a silicone treated filter or a layer of a porous material ($MgSO_4$) to remove elemental selenium. Toluene (25 ml) was added and the solution concentrated *in vacuo* at 20 °C to *ca.* 10 ml. The solution was transferred to a centrifuge tube, cooled in acetone–dry-ice and the precipitated crystals isolated by centrifugation and dried over conc. sulfuric acid in a desiccator. *4,4-Diethylselenosemicarbazide,* 76 % yield, m.p. 85–88 °C. Found: C, 30.96; H, 6.84; N, 21.87. Calc. for $C_5H_{13}N_3Se$: C, 30.77; H, 6.67; N, 21.54.

Preparation and properties of 5-diethylamino-1,2,3,4-selenatriazole. Path a. Bis(*N,N*-diethylselenocarbamoyl)selenide (*1*) (1 mmol) was suspended in methanol (20 ml), ammonium azide (2 mmol) was added and the mixture left for 24 h at room temperature with stirring and protected against light. Water (20 ml) was added and the precipitated triselenide removed by filtration. The solution was saturated with sodium chloride, transferred to a separating funnel and extracted with ether (2×10 ml). The combined ether extracts were filtered through a silicone treated filter to remove elemental selenium dried over $MgSO_4$ at 0 °C followed by evaporation of the solvent *in vacuo* at 0 °C and protected against light. 85 % yield, oil. MS: 206.0122 ($M^{\cdot+}$, 0.62 %, calc. for $C_5H_{10}N_4Se$: 206.0070), 178 ($M^{\cdot+}-N_2$, 1.9 %), 122 ($C_2H_5CHSe^{\cdot+}$, 2.4 %), 98 ($(C_2H_5)_2NCN^{\cdot+}$, 100 %), 83 ($C_2H_5N(=CH_2)CN^+$, 80 %), 70 (C_2H_5NHCN, 11 %), 69 (9.2 %), 55 (54 %), 42 (3.8 %), 41 (4.6 %). NMR ($CDCl_3$), δ 1.40 (CH_3), 3.68 (CH_2) IR: Lack of azide band in the heterocumulene region (*ca.* 1800–2400 cm^{-1}). UV (CCl_4): λ 278 nm, ε 5875±2 %. The decomposition of the selenatriazole in CCl_4 at room temperature to diethylcyanamide was monitored by NMR and a half-life of 8 days was calculated. Diethylcyanamide was identified by comparison with authentic

material. The selenatriazole may be submitted to column chromatography (silica gel) with ether as eluent.

Preparation of 5-methyl(phenyl)amino-1,2,3,4-selenatriazole. Bis(methyl(phenyl)selenocarbamoyl)selenide (0.25 mmol) was dissolved in methanol–dioxane (1:1), ammonium azide (1.66 mmol) was added and the mixture left for 24 h at 0 °C. The solvent was removed *in vacuo* with protection against light. The remains were extracted with ether, followed by drying over $MgSO_4$ at 0 °C, and the solvent removed *in vacuo* at 0 °C to give an oil. NMR (CCl_4): Bands are observed at δ 3.34 and 3.66 (ratio *ca.* 3:1) and around δ 7.0–7.5 (phenyl). The band at δ 3.66 gradually disappears at room temperature and is tentatively assigned to 5-methyl(phenyl)amino-1,2,3,4-selenatriazole. The cyanamide was identified by comparison with authentic material.

Aza-transfer reaction. Path b. The mono or disubstituted selenosemicarbazide (0.1 mmol) was suspended in methanol (10 ml) cooled to 0 °C and protected against light. Benzenediazonium tetrafluoroborate (0.11 mmol) was added gradually as a solid or added slowly as a methanol suspension. The reaction mixture was stirred for 30 min, water (20 ml) was added, the solution was saturated with sodium chloride, transferred to a separating funnel and extracted with ether (10×2 ml). The combined ether extracts were dried over $MgSO_4$ at 0 °C and filtered through a silicone treated filter to remove elemental selenium. The solvent was removed *in vacuo* at 0 °C.

Diazotized sulfanilic acid prepared according to literature [4] may be used instead of benzenediazonium tetrafluoroborate. It is used in 10 % excess as a suspension in methanol.

5-Diethylamino-1,2,3,4-selenatriazole was prepared in this manner with benzenediazonium tetrafluoroborate in 70 % yield.

On attempted preparation of 5-cyclohexylamino-1,2,3,4-selenatriazole, an oil was obtained which exhibited a strong IR absorption ($CHCl_3$) at 2200 cm^{-1} indicating formation of cyclohexylisoselenocyanate. A GLC–MS investigation demonstrated the presence of cyclohexylisoselenocyanate (and absence of cyclohexylcyanamide) and of diphenylselenide while MS directly on the oil showed the presence of diphenyldiselenide as well. Cyclohexylisoselenocyanate is assumed to be formed from 5-cyclohexylamino-1,2,3,4-selenatriazole but we have not been able to demonstrate its presence in the oil obtained (IR and ^1H NMR).

A similar result was obtained on attempted preparation of 5-benzylamino-1,2,3,4-selenatriazole. The isolated oil was shown to contain benzylisoselenocyanate identical (TLC and ^1H NMR) with an authentic sample.

Acknowledgement. We thank Dr. J. Øgaard Madsen for recording the GLC-mass spectra.

REFERENCES

1. Jensen, K. A. and Pedersen, C. *Adv. Heterocycl. Chem. 3* (1964) 263.
2. Holm, A. *Adv. Heterocycl. Chem. 20* (1976) 145.
3. Henriksen, L. *Synthesis* (1982) 771.
4. Stanovnik, B., Tisler, M. and Valencic, B. *Org. Prep. Proced. 10* (1978) 59.
5. Klayman, D. L. and Günther, W. H. H. *Organic Selenium Compounds: Their Chemistry and Biology*, Wiley, New York 1973.
6. Esperås, S., Husebye, S. and Rolandsen, Å. *Acta Chem. Scand. A 29* (1975) 608.

Received October 6, 1982.