Preparation and Characterisation of *N,N*-Disubstituted 2-Amino-5*H*-selenophenes*

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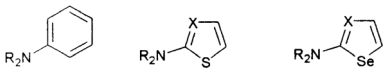
Dedicated to Prof. Willi Kantlehner on the occasion of his 60th birthday

The reaction of *N,N'*-persubstituted selenoacrylamides with alkyl bromoacetates gives rise to the formation of alkyl derivatives of *N,N*-disubstituted 2-aminoselenophene-5-carboxylates which can be transformed by saponification into corresponding 5-carboxylic acids. These compounds decompose by heating under formation of hitherto unknown *N,N*-disubstituted 2-amino-5*H*-selenophenes their spectral and chemical properties were outlined.

Key words: 2-Aminoselenophenes, Heterocyclisation, Decarboxylation, Heterocyclic Azo Dyes, Methine Dyes

In the last three decades *N,N*-disubstituted 2-aminothiophenes **2** and 2-amino-1,3-thiazoles **3** received a lot of interest. As heterocyclic analogues of the well-known *N,N*-disubstituted anilines **1**, which are important starting compounds for the synthesis of organic dyes [1], they have also been used as versatile precursors for the preparation of different types of organic dyes. Thus, *N,N*-disubstituted 2-aminothiophenes **2** could by successfully transformed, especially if unsubstituted at their 5-position, into, *e. g.*, azo dyes [2], methine [3] and azomethine dyes [4], or squarylium [5] and croconium dyes [6]. Recently these heterocycles were used for the preparation of a variety of stilbenoid dyes with high non-linear optical properties [7]. Analogously, *N,N*-disubstitued 2-aminothiazoles **3** [8] have been transformed into corresponding azo dyes [9], methine and azamethine dyes [4], as well as into squarylium dyes [10]. Very recently *N,N*-disubstitued 2-aminoselenazoles **5** have also found attention as starting materials for the synthesis of different types of dyes [11], namely azo dye [9], methinum dyes [4], and squarylium dyes [12] (Scheme 1).



Scheme 1.

For the use of the mentioned heterocyclic amines **2**, **3**, and **5** as dye precursors, a simple access to these compounds was an important precondition. Usually these amines could be prepared from simple thioacetamides, thiourea or selenourea precursors, respectively, and halomethyl ketones using the well-known Hantzsch route [13, 14]. For the *N,N*-disubstituted 2-aminothiophenes **2** a route starting from secondary amines and 2-mercaptothiophene [15] or 2-bromothiophene [16] was also convenient.

We found, however, that both methods could not be applied for the synthesis of *N,N*-disubstituted 2-aminoselenophenes **4**. Therefore, these seleno-containing heterocyclic amines are unknown as yet and constitute the missing link in the series of heterocylic aniline analogues **2** – **5**. Only few *N,N*-disubstituted 2-aminoselenophenes substituted with strong electron acceptor moieties in their 5-position have been prepared very recently by starting from *N,N'*-persubstituted selenoacrylamides **6** [17]. These compounds which were easily available from *N,N'*-persubstituted 1-chlorovinamidinium salts by reaction with sodium selenide [18] were allowed to react with acceptor-substituted halomethyl compounds **7** to yield *N,N*-

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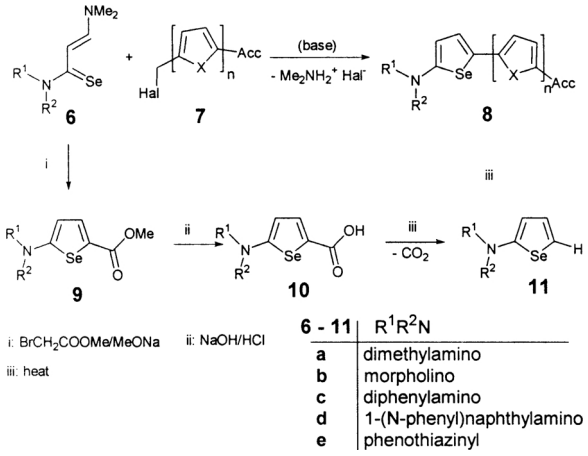
Table 1. Melting points and ^{1}H NMR data of the compounds **10** and **11** prepared.

Entry	R^1R^2N	Yield (%)	M. p. (°C)	^{1}H NMR, δ-values, measured in [D6]-DMSO for **10** and in $CDCl_3$ for **11** (ppm)
10a	Dimethylamino	87	122 – 124	2.99 (s, 6H, NCH_3), 5.86 (d, 1H, CH), 7.62 (d, 1H, CH), 11.67 (s, 1H, OH)
10b	Morpholino	88	150 – 152	3.18 (t, 4H, NCH_2), 3.73 (t, 4H, OCH_3), 5.86 (d, 1H, CH), 7.62 (d, 1H, CH), 11.76 (s, 1H, OH)
10c	Diphenylamino	87	149 – 151	6.33 (d, 1H, CH), 7.25 (m, 6H, CH), 7.40 (m, 4H, CH), 7.62 (d, 1H, CH), 12.49 (s, 1H, OH)
10d	1-(*N*-Phenyl)-naphthylamino	72	137 – 139	6.13 (d, 1H, CH), 7.21 (m, 4H, CH), 7.41 – 7.51 (m, 5H, CH), 7.81 – 7.94 (m, 3H, CH)
10e	Phenothiazinyl	90	138 – 142	6.77 (d, 1H, CH), 7.18 – 7.24 (m, 2H, CH), 7.29 – 7.35 (m, 2H, CH), 7.37 – 7.42 (m, 4H, CH), 7.73 (d, 1H,CH)
11a	Dimethylamino	64	oil	2.94 (s, 6H, NCH_3), 5.89 (dd, 1H, CH), 6.99 (q, 1H, CH), 7.09 (dd, 1H, CH)
11b	Morpholino	62	oil	3.10 (t, 4H, NCH_2), 3.82 (t, 4H, OCH_2), 6.19 (dd, 1H, CH), 7.02 (q, 1H, CH), 7.26 (dd, 1H, CH)
11c	Diphenylamino	70	108 – 110	6.77 (dd, 1H, CH), 7.04 – 7.12 (m, 7H, CH), 7.28 – 7.34 (m, 4H, CH), 7.79 (dd, 1H, CH)
11d	1-(*N*-Phenyl)-naphthylamino	78	88 – 91	6.72 (dd, 1H, CH), 6.87 – 6.95 (m, 3H, CH), 7.01 (q, 1H, CH), 7.16 – 7.21 (m, 2H, CH), 7.44 – 7.60 (m, 6H, CH), 7.67 (dd, 1H, CH), 7.91 – 8.01 (m, 3H, CH)
11e	Phenothiazinyl	94	90 – 94	6.20 (dd, 2H, CH), 6.96 (m, 2H, CH), 7.05 – 7.14 (m, 4H, CH), 7.30 – 7.35 (m, 2H, CH), 8.23 (dd, 1H)

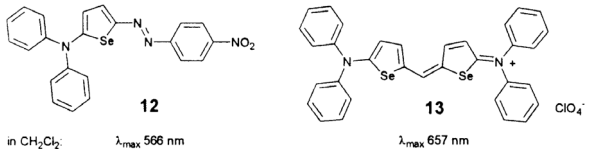


Scheme 2.

disubstituted 2-aminoslenophenes of the general structure **8** [19].

Now we found that the 5-methoxycarbonyl derivatives **9** of such 2-aminoselenophenes, prepared by reaction of the *N,N'*-persubstituted selenoacrylamides **6** with methyl bromoacetate as described in ref. [19], can be used to prepare the 5*H*-substituted parent compound. To this end, these methyl 2-aminoselenophene-5-carboxylates **9** were transformed by reaction with aqueous/methanolic sodium hydroxide and subsequent addition of mineral acid into the corresponding carboxylic acids **10** from which the hitherto unknown *N,N*-disubstituted 2-amino-5*H*-selenophenes **11** were available by heating at their melting points. Analogously to the behaviour of the *N,N*-disubstituted 2-aminothiophene-5-carboxylic acids [20], these carboxylic acids **10** [21] decompose under elimination of carbon dioxide to give rise to the formation of the desired compounds **11** in mostly moderate yield. The *N,N'*-disubstituted 2-amino-5*H*-selenophenes **11** so prepared (see Table 1) are colourless or pale yellow coloured solids which can be stored in a closed vessel under nitrogen without decomposition. Their constitution was confirmed by means of elemental analyses and spectroscopic data. Thus, the *N,N'*-disubstituted 2-aminoselenophenes **11** exhibit in their ^{1}H NMR spectra characteristic signals at $\delta = 2.9 - 3.9$ and $5.9 - 8.0$ ppm. Whereas the signals in the first range arise from the protons at the *N*-alkyl groups, the signals in the second range can be attributed to the protons at their selenophene and, as far as present, at their *N*-aryl moieties.

It is worth mentioning that there is a significant difference between the spectral pattern of the *N,N'*-disubstituted 2-aminoselenophenes **11** and their 5-



Scheme 3.

carboxylic acid precursors **10**. Whereas the carboxylic acids **10** exhibit, analogously to their alkyl carboxylates **9** [16], two characteristic doublets at about 6.0 and 7.7 ppm with coupling constants $J = 4.5$ Hz, the 5*H*-substituted 2-aminoseleophenes **11** exhibit three multiplets between 5.9 and 7.9 ppm with coupling constants $J = 1.2$, 3.9, and 6.0 Hz. Although in the 2-aminoselenophenes **11** one of these multiplets is superimposed by the multiplets of the aryl protons, it can be recognised that the chemical shifts of the selenophene protons are significantly influenced by the type of amino substituents. Thus, for the *N*-alkyl-substituted 2-aminoselenophenes **11a** and **11b** these multiplets were found between 5.9 and 7.3 ppm whereas for the *N*-aryl-substituted 2-aminoselenophenes **11c** and **11d** these multiplets were found at considerably lower fields. This fact indicates that the electron-donating effect of the arylamino substituents on the selenophene moiety is significantly smaller than the one of the *N*-alkyl substituents.

As expected, the new *N*,*N*-disubstituted 2-aminoselenophenes **11** and their carboxylic acid precursors **10** can be used as versatile starting materials for the preparation of organic dyes. Thus, with arene diazonium salts or reactive formyl derivatives they can be transformed, as exemplified by compounds **12** and **13**, into deeply coloured compounds. Details on these reactions, which were performed accordingly to reported methods for preparing corresponding 2-aminothiophene dyes [2, 4], and on the properties of the compounds so obtained will be published in a forthcoming paper soon.

Experimental Section

Melting points: Boetius heating-table, uncorrected. ^{1}H NMR: Varian 300 Gemini (300 MHz). Elemental analyses: LECO CHNS 932.

Preparation of N,N-disubstituted 2-aminoselenophenes **11** *and their 5-carboxylic acid precursors* **10** *(General procedure)*

The methyl derivative of a *N*,*N*-disubstituted 2-aminoselenophene-5-carboxylate **9** (0.01 mol), prepared according to ref. [19], was refluxed in methanol (50 ml) containing a concentrated aqueous sodium hydroxide solution (0.015 mol) for 30 min. After cooling at room temperature the mixture was filtrated and, subsequently acidified with diluted HCl. The 2-aminoselenophene-5-carboxylic acid **10** precipitated was isolated by filtration and dried at 50 °C. By heating at its melting point the acids **10** decompose to yield the corresponding *N*,*N*-disubstituted 2-aminoseleophenes **11** as oils which crystallise after cooling at room temperature and triturating with some methanol or diethyl ether. Physical data of compounds **10** and **11** are given in Table 1.

Compound **11a**: C_6H_9NSe (175.0): calcd. C 41.39, H 5.21, N 8.05; found: C 41.03, H 5.33, N 8.08.

Compound **11b**: $C_8H_{11}NOSe$ (216.1): calcd. C 44.46, H 5.13, N 6.48; found: C 44.09, H 5.22, N 6.66.

Compound **11c**: $C_{16}H_{13}NSe$ (299.0): calcd. C 64.43, H 4.39, N 4.70; found: C 64.64, H 4.42, N 4.58.

Compound **11d**: $C_{20}H_{15}NSe$ (349.0): calcd. C 68.97, H 4.34, N 4.02; found: C 69.39, H 4.34, N 4.15.

Compound **11e**: $C_{16}H_{11}NSSe$ (229.0): calcd. C 58.54, H 3.38, N 4.27; found: C 59.02, H 3.28, N 4.25.

Methyl 2-[(*N*-phenyl-1-naphthylamino]selenophene-5-carboxylate (**9d**), the precursor of compound **10d**, has the following physical data: m.p. 98 – 100 °C. – ^{1}H NMR ($CDCl_3$): $\delta = 3.07$ (s, 3H, OCH_3), 6.42 (d, 1 H, CH), 7.27 – 7.38 (m, 6 H, CH), 7.62 (m, 2 H, CH), 7.66 – 7.73 (m, 4H, CH).

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