A Simple Route to $N,N$-Disubstituted Selenoureas from $N,N$-Disubstituted Cyanamides

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Abstract: $N,N$-Disubstituted selenoureas 4 can be obtained in satisfactory yields by addition of an acid to a mixture of freshly prepared sodium selenide and $N,N$-disubstituted cyanamides 5.

Key words: $N,N$-disubstituted selenoureas, $N,N$-disubstituted cyanamides, nucleophilic substitution, selenium

In analogy to $N,N$-disubstituted thioureas 3, $N,N$-disubstituted selenoureas 4 are versatile starting materials for the preparation of different types of heterocycles. For instance, they can be used for the synthesis of $N,N$-disubstituted 2-aminoselenazoles. 2 Recently, these compounds have received a special interest as starting materials for a variety of functional dyes useful for, e.g., measuring the solvent polarity, 3–5 manufacturing electrophotographic data recording systems, 6,7 or for preparing compounds absorbing infrared radiation. 8

Compared to their $N,N$-disubstituted sulfur analogues 3, $N,N$-disubstituted selenoureas 4 can not be prepared by heating the corresponding ammonium selenocyanates 2. 2 Similarly, they can not also be prepared, analogous to their sulfur analogues 3, by hydrolysis of acylselenoureas 9 which are available by reaction of alkali or ammonium selenocyanides 2 with acyl chlorides 6 and subsequent reaction of the primarily formed acyl isoselenocyanates 8 with amines 10 (Scheme 1). The $N,N$-disubstituted selenoureas 4 can be prepared, however, from $N,N$-disubstituted thioureas 3 via their alkyl derivatives, 11 or from $N,N$-disubstituted cyanamides 5 by reaction with dihydrogensenide that has been generated from Al 2 Se 3 by hydrolysis. 2 Although both methods seem, at first glance, rather simple they require the use of an extremely toxic reagent.

Now, we have found a more simple method for obtaining $N,N$-disubstituted selenoureas 4. It also starts from $N,N$-disubstituted cyanamides, and proceeds by the use of Na 2 Se or NaHSe avoiding the free gaseous H 2 Se (Scheme 1). These reagents can be prepared, as generally known, very simply from elemental selenium by reaction with sodium borohydride. 12 For carrying out the reaction, it is only necessary to add slowly an equivalent amount of a mineral acid, like hydrochloric acid, to a mixture of the components. Instead of the acid, a suitable ammonium salt, such as pyridinium hydrochloride, can also be used. The reaction has some analogies to the reported preparation of selenobenzamides from benzonitriles 13–15 as well as to the preparation of $N,N$-disubstituted selenoureas 4 from $N,N$-disubstituted cyanamides and LiAlSeH. 16

For obtaining a satisfactory yield of the $N,N$-disubstituted selenoureas 4, it is recommendable to let the reaction mixture stand overnight after the addition of acid. The products formed can be isolated by usual work-up (see experimental).

Melting points were determined by means of a Differential Scanning Calorimeter (Mettler, Toledo) with a heating rate of 5 °C/min. The NMR spectra were recorded with a Varian Gemini 300 MHz spectrometer. The elemental analyses were estimated by means of a LECO analyser CHNS 932.

$N,N$-Disubstituted Selenoureas 4; General Procedure
Method A: Under inert gas conditions, NaBH 4 (8.1 g, 215 mmol) was slowly added to a cooled and stirred mixture of elemental Se (15.8 g, 200 mmol) in EtOH (200 mL). After decolourisation of the reaction mixture, a $N,N$-disubstituted cyanamide 5 (100 mmol), followed by pyridine hydrochloride (46.2 g, 400 mmol), were added slowly and the mixture was stirred overnight. The reaction was quenched by addition of H 2 O (500 mL) and the product formed was extracted with CH 2 Cl 2 (300 mL). The CH 2 Cl 2 solution was dried
and the solvent evaporated in vacuo to give a crystalline product. It was recrystallised from toluene under N₂.

**Method B (In Analogy to Ref.13):** A N,N-disubstituted cyanamide 5 (100 mmol) was added to a freshly prepared solution of NaSe (200 mmol) in EtOH (200 mL) under an inert gas atmosphere. After adding pyridine (32.4 mL, 400 mmol), aq 2 M HCl (100 mL) was slowly added to the boiling mixture over a period of 4 h. The reaction mixture was quenched by addition of H₂O (500 mL) and worked up as before.

**N,N-Dimethylselenourea (4a)**
Yield: 50–55%; mp 174 °C (Lit.: mp 173 °C).

13C NMR (DMSO-d₆): δ = 177.9 (CSe).

**N,N-Diethylselenourea (4b)**
Yield 40–45%; mp 122 °C (Lit.: mp 121 °C).

13C NMR (CDCl₃): δ = 177.1 (CSe).

**N,N-Dibenzylselenourea (4c)**
Yield: 45–50%; mp 141 °C (Lit.: mp 139 °C).

13C NMR (CDCl₃): δ = 181.6 (CSe).

**N-(Selenocarbamido)morpholine (4d)**
Yield 30–35%; mp 201 °C (Lit.: mp 195 °C).

13C NMR (DMSO-d₆): δ = 178.2 (CSe).

**N-(Selenocarbamido)pyrrolidine (4e)**
Yield: 49–50%; mp 213 °C (Lit.: mp 212 °C).

13C NMR (CDCl₃): δ = 173.7 (CSe).

**N-(Selenocarbamido)piperidine (4f)**
Yield: 35–40%; mp 147 °C (Lit.: mp 147 °C).

13C NMR (CDCl₃): δ = 177.8 (CSe).

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**References**