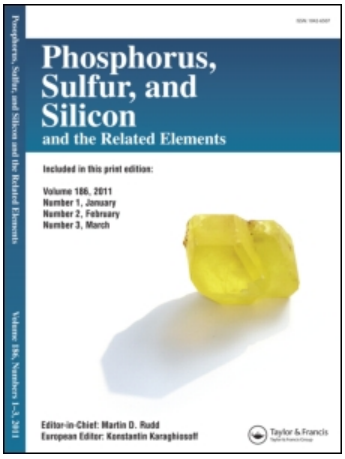

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PREPARATION AND CHARACTERISATION OF *N,N*-DISUBSTITUTED 2-AMINO-SELENAZOLES

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As a result of checking suited methods for preparing *N,N*-disubstituted 2-amino-selenazoles **14** as a nearly unknown class of highly reactive selenazoles a simple route starting from *N,N*-disubstituted selenoureas **12** has been elaborated and used for the synthesis of a series of these compounds. The necessary selenium-containing starting compounds **12** are available from *N,N*-disubstituted cyanamides **18** and hydrogen selenide.

Keywords: *N,N*-disubstituted cyanamides; *N,N*-disubstituted selenoureas; *N,N*-disubstituted 2-amino-selenazoles; Hantzsch method

INTRODUCTION

In the last three decades *N,N*-disubstituted 2-amino-thiophenes **2** and 2-amino-thiazoles **3** have received much interest. As heteroanalogues of *N,N*-disubstituted anilines **1**, which are important starting compounds for preparing organic dyes,[1] they have been used as versatile educts for preparing different types of organic dyes also. Thus, *N,N*-disubstituted 2-amino-thiophenes **2** can be successfully transformed, especially if they are unsubstituted in their 5-position, e.g., into azo dyes,[2] methine dyes,[3] or squarylium and croconium dyes.[4] Analogously, *N,N*-disubstituted 2-amino-thiazoles **3** have been transformed into corresponding azo dyes,[5] methine and azomethine dyes,[6] or squarylium dyes.[7]

In contrast to the above mentioned thiophenes **2** and thiazoles **3** *N,N*-disubstituted selenazoles **4** have found, surprisingly, no such attention hith-

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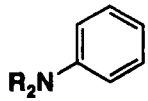

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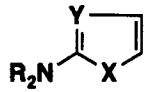


2 - 4

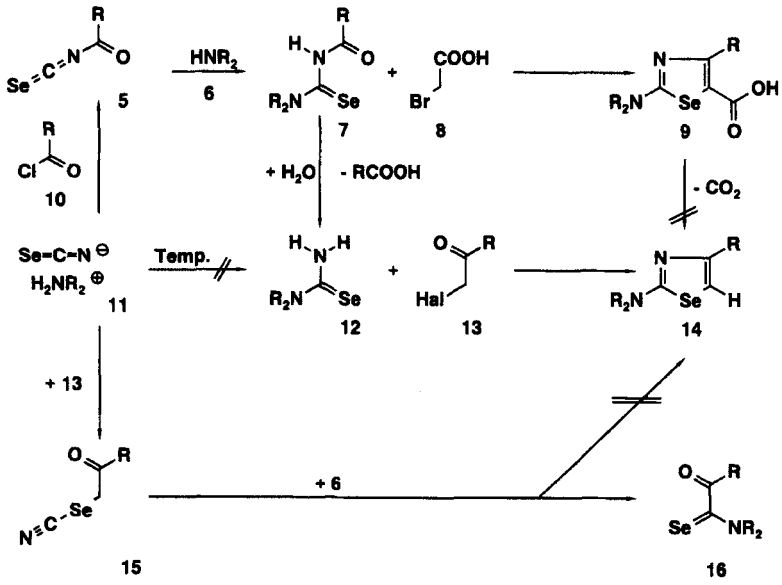
	X	Y
2	S	CH
3	S	N
4	Se	N

SCHEME 1

erto. Obviously, the failure of simple routes to prepare these heterocyclic compounds **4** seems to be the main reason for this lack of attention. Indeed, only few *N,N*-disubstituted 2-amino-5H-selenazoles **4** have been described in the literature until now.[8] As starting compounds for their reported synthesis *N,N*-disubstituted selenoureas have been used. The synthetic route for the preparation of these educts is accompanied, however, with the use of unpleasant hydrogen selenide.

RESULTS AND DISCUSSION

For finding a more convenient route to *N,N*-disubstituted selenoureas **12,** which are only sparsely documented in the literature,[8,9] and, hence, to elaborate a simple way to *N,N*-disubstituted 2-amino-selenazoles **14** by using the well-known Hantzsch route,[10] we tried to adapt, at first, methods which were useful for a hydrogen selenide free synthesis of these compounds. Thus, we tried to prepare the *N,N*-disubstituted selenoureas **12,** accordingly to the well-known Wöhler urea and thiourea synthesis, by heating dialkylammonium selenocyanates **11.** However, the desired compounds **12** are, analogously to *N,N*-disubstituted thioureas,[11] not synthesizable by this route. Therefore, the hydrolysis of *N,N*-disubstituted *N'* -acyl-selenoureas **7,** easily available by reaction of alkali or ammonium selenocyanates **11** with acyl chlorides **10** followed by the reaction of the primarily formed acylisoselenocyanates **5** with secondary amines **6,**[12] with aqueous bases or mineral acids was studied here. However, other than in the case of *N*-monosubstituted *N'*-acyl-selenoureas, which can be cleaved under these conditions into *N*-monosubstituted selenoureas,[13] the same reaction with *N,N*-disubstituted *N'*-acyl-selenoureas **7** failed.

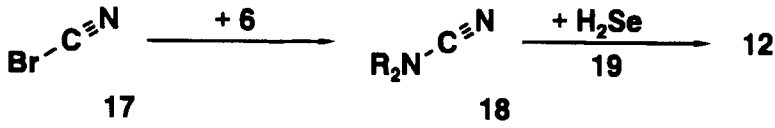


SCHEME 2

A similar negative result was obtained by trying to decarboxylate 2-dialkylamino-selenazole-5-carboxylates **9,** which are available, analogously to their thiazole analogues,[14] from the *N,N*-disubstituted *N'*-acyl-selenoureas **7** by reaction with haloacetic acids **8** or their derivatives. Other than in the sulphur series[15] these compounds **9** decompose by heating, forming only tar and elemental selenium.

Furthermore, a negative result has been obtained in course of the reaction of selenocyanatomethyl ketones **15** with secondary amines **6.** In contrast to the sulphur series,[16] instead of the desired 2-dialkylamino-selenazoles **14,** only unsuitable acylselenoamides **16** were obtained.[17]

Hence, as a practicable method for preparing *N,N*-disubstituted selenazoles **14** only the Hantzsch route remains. It requires as educts, however, *N,N*-disubstituted selenoureas **12.** As mentioned above, these compounds are only available from *N,N*-disubstituted cyanamides **18** and hydrogen selenide **19.** The later reagent is available from aluminium selenide and aqueous mineral acid.[18] The cyanamides **18** are available either by reaction of cyanogen bromide **17** with secondary amines **6**[19] or by alkylation of the parent cyanamide.[20]



SCHEME 3

For the transformation of the *N,N*-disubstituted cyanamides **18** into corresponding *N,N*-disubstituted selenoureas **12,** hydrogen selenide **19** was injected in presence of ammonia into their ethanolic solution at slightly elevated temperature.

The *N,N*-disubstituted selenoureas **12** so prepared are listed in Table I. In all cases, they were obtained as crystalline solids in moderate yields.

The structure of the selenoureas **12** follows from their elemental analytic (see Table I) as well as from their spectroscopic data (see Table II). Thus, the *N,N*-disubstituted selenoureas **12** exhibit characteristic and intense signals in their IR spectra in the range at about 3430 to 3130 cm^{-1} and at about 1630 to 1340 cm^{-1}. Whereas the first set of signals can be attributed to their NH_2 group, the other one can be attributed to their N-C-Se moiety.

In the ^1H NMR spectra of the *N,N*-disubstituted selenoureas **12** the NH_2 protons give rise to broad peaks; their positions varied between 6.00 to 8.00 ppm.

For preparing *N,N*-disubstituted 2-amino-selenazoles **14,** the *N,N*-disubstituted selenoureas **12** were refluxed in ethanol with a stoichiometric amount of an appropriate halomethyl ketone **13** (Hal = Cl or Br).

The *N,N*-disubstituted 2-amino-selenazole hydrobromides **14·HBr** primarily formed were not isolated, in general, but directly transformed into their free bases **14** by addition of triethylamine to the reaction mixture. After addition of water, crystalline products were isolated from the resulting mixture by filtration. Non-crystalline products were isolated by distillation under reduced pressure after their extraction with diethyl ether from the reaction mixture.

All *N,N*-disubstituted 2-amino-selenazoles **14** so prepared are listed in Table III. Usually, they could be isolated in satisfactory yields. The selenazole **14o,** previously described as oil,[8] was even obtained as crystalline product.

The *N,N*-disubstituted 2-amino-selenazoles **14** were unambiguously characterised by their elemental analytic as well as IR and ^1H NMR spectral data. Some of these data are recorded in Tables III and IV.

TABLE I Characteristic data of the synthesized N,N-disibstituted selenoureas **12**

Nr.	R_2N	*Yield [%]*	*m.p. [°C] (Lit. m.p.)*	*Formula (m.w.)*	*calcd. found*	*C*	*H*	*N*
12a	Me_2N	35–40	173 (169 – 170)[8]	$C_3H_8N_2Se$ (151.1)		23.85 23.86	5.34 5.16	18.54 18.17
12b	Et_2N	45–50	121 (121 – 124)[8]	$C_5H_{12}N_2Se$ (179.1)		33.53 33.76	6.75 6.66	15.64 15.28
12c	Bz_2N	53–55	139	$C_{15}H_{16}N_2Se$ (303.3)		59.41 59.38	5.32 5.34	9.24 8.81
12d	NMePh	40–45	149	$C_8H_{10}N_2Se$ (213.1)		45.08 45.85	4.73 4.78	13.14 12.91
12e	Morpholino	30–35	195 dec.	$C_5H_{10}N_2OSe$ (193.1)		31.10 31.07	5.22 5.28	14.51 14.25
12f	Pyrrolidino	40–45	212 dec.	$C_5H_{10}N_2Se$ (177.1)		33.91 33.88	5.69 5.62	15.82 15.42
12g	Piperidino	35–40	147	$C_6H_{12}N_2Se$ (191.1)		37.70 38.04	6.33 6.38	14.66 14.36

TABLE II Characteristic spectral data of the synthesized *N,N*-disibstituted selenoureas **12**

Nr	R_2N	*^{1}H-NMR, δ-values, measured in [D_6] DMSO (assignment)*	*IR, values in [cm^{-1}], measured in Nujol*						
			ν_{NH2}					ν_{NCSe}	
12a	Me2N	3.16 (m, 6H, NCH_3), 7.57 (*broad*, 2H, NH_2)	3361	3261	3154	1615	1551	1415	1349
12b	Et_2N	1.08 (t, 6H, CH_3), 3.60 (*broad*, 4H, NCH_2), 7.54 (broad, 2H, NH_2)	3337	3279	3175	1625	1531	1437[b])	1357
12c	Bz_2N	4.6 – 5.2 (*broad*, 4H, NCH_2), 7.26 – 7.39 (m, 10H, CH_{Ar}), 8.04 (*broad*, 2H, NH_2)	3422	3255	3153	1616	1504	1453[b])	1352
12d	NMePh	3.78 (s, 3H, NCH_3), 6.08 (*broad*, 2H, NH_2), 7.24 – 7.52 (m, 5H, CH_{Ar}) [a])	3363	3269	3164	1617	1588	1487[b])	1364
12e	Morpholino	3.56 (m, 4H, NCH_2), 3.79 (*broad*, 4H, OCH_2), 7.90 (*broad*, 2H, NH_2)	3402	3313	3211	1627	1521	1444	1344
12f	Pyrrolidino	1.83 (m, 2H, CH_2), 2.12 (m, 2H, CH_2), 3.33 (t, 2H, NCH_2), 3.90 (t, 2H, NCH_2), 5.95 (*broad*, 2H, NH_2) [a])	3289	3258	3136	1619	1523	1465	1354
12g	Piperidino	1.68 (s, 6H, CH_2), 3.82 (*broad*, 4H, NCH_2), 6.13 (*broad*, 2H, NH_2) [a])	3302	3267	3157	1621	1521	1465	1369

[a]) measured in $CDCl_3$. [b]) broad.

TABLE III Characteristic data of the synthesized *N,N*-disibstituted 2-amino-selenazoles **14**

Nr.	*R2N*	*R*	*Yield [%]*	*m.p. [°C]; b.p. [°C] /p [Torr]*	*Formula (m.w.)*	*calcd found*	*C*	*H*	*N*
14a	Me2N	C_6H_5	35–40	144–146/1.0	$C_{11}H_{12}N_2Se$		52.60	4.82	11.15
					(251.2)		52.80	4.71	10.82
14b	Et2N	C_6H_5	45–50	153 – 154/1.0	$C_{13}H_{16}N_2Se$		55.92	5.78	10.03
					(279.3)		55.99	5.63	10.11
14c	Bz_2N	C_6H_5	50–55	109	$C_{23}H_{20}N_2Se$		68.48	5.00	6.94
					(403.4)		68.53	5.05	6.73
14d	NMePh	C_6H_5	55–60	88	$C_{16}H_{14}N_2Se$		61.35	4.50	8.94
					(313.3)		61.28	4.43	8.93
14e	Morpholino	C_6H_5	60–65	88	$C_{13}H_{14}N_2OSe$		53.25	4.81	9.55
					(293.2)		53.25	4.77	9.28
14f	Pyrrolidino	C_6H_5	55–60	56	$C_{13}H_{14}N_2Se$		56.32	5.09	10.10
					(277.2)		56.65	5.19	9.82
14g	Piperidino	C_6H_5	60–65	83	$C_{14}H_{16}N_2Se$		57.73	5.54	9.62
					(291.3)		58.15	5.30	9.69
14h	Me2N	*t*-Bu	65–70	70 – 72/1.0	$C_9H_{16}N_2Se$		46.76	6.98	12.12
					(231.2)		47.29	6.76	11.83
14i	Et2N	*t*-Bu	55–60	94 – 95/2.5	$C_{11}H_{20}N_2Se$		50.96	7.78	10.81
					(259.3)		51.11	7.45	10.57
14j	Bz_2N	*t*-Bu	45–50	198 – 200/1.0	$C_{21}H_{24}N_2Se$		65.79	6.31	7.31
					(383.4)		65.65	6.02	7.04
14k	NMePh	*t*-Bu	55–60	131–132/0.7	$C_{14}H_{18}N_2Se$		57.34	6.19	9.55
					(293.3)		57.39	6.24	9.73

Nr.	*R2N*	*R*	*Yield [%]*	*m.p. [°C]; b.p. [°C] /p [Torr]*	*Formula (m.w.)*	*calcd found*	*C*	*H*	*N*
141	Morpholino	*t*-Bu	35–40	124–126/2.0	$C_{11}H_{18}N_2OSe$ (273.2)		48.35 48.38	6.64 6.58	10.25 10.50
14m	Pyrrolidino	*t*-Bu	55–60	115–116/1.5	$C_{11}H_{18}N_2Se$ (257.2)		51.36 51.38	7.05 7.21	10.89 10.78
14n	Piperidino	*t*-Bu	40–45	120–122/2.0	$C_{12}H_{20}N_2Se$ (271.3)		53.13 53.16	7.43 7.40	10.33 10.79
14o	Me2N	CH_3	60–65	47; 65/1.0	$C_6H_{10}N_2Se$ (189.1)		38.11 38.12	5.33 5.28	14.81 14.42
14p	Et_2N	CH_3	65–70	70 – 72/1.0	$C_8H_{14}N_2Se$ (217.2)		44.24 44.74	6.50 6.77	12.90 12.75
14q	Bz_2N	CH_3	60–65	81	$C_{18}H_{18}N_2Se$ (341.3)		63.34 63.55	5.32 5.27	8.21 8.71
14r	Morpholino	CH_3	40–45	56; 110 – 112/1.0	$C_8H_{12}N_2OSe$ (231.2)		41.57 41.53	5.23 5.24	12.12 11.72
14s	Pyrrolidino	CH_3	50 – 55	80	$C_8H_{12}N_2Se$ (215.2)		44.66 44.99	5.62 5.61	13.02 12.77
14t	Piperidino	CH_3	60 – 65	99 – 102/1.0	$C_9H_{14}N_2Se$ (229.2)		47.17 46.97	6.16 5.94	12.22 11.85
14u	NMePh	CH_3	45 – 50	47	$C_{11}H_{12}N_2Se$ (251.2)		52.60 52.43	4.82 4.82	11.15 11.11
14v	Pyrrolidino	H	10 – 15	67; 108 – 110/1.0	$C_7H_{10}N_2Se$ (201.1)		41.80 41.51	5.01 5.12	13.93 13.73

TABLE IV Characteristic spectral data of the synthesized N,N-disubstituted 2-amino-selenazoles **14**

Nr.	R_2N	*R*	*IR*, ν_{CN} [cm^{-1}][a]	^{1}*H-NMR, δ-values, in* $CDCl_3$ *(assignment)*
14a	Me2N	C_6H_5	1567[b]	3.09 (s, 6H, NCH_3), 7.61 (s, 1H, CH_{Het}), 7.26 – 7.88 (m, 5H, CH_{Ar}) [c]
14b	Et_2N	C_6H_5	1551[b]	1.21 (t, 6H, CH_3), 3.47 (q, 4H, NCH_2), 7.26–7.87 (m, 5H), 7.55 (s, 1H, CH_{Het}) [c]
14c	Bz_2N	C_6H_5	1548	4.75 (s, 4H, NCH_2), 7.28–7.87 (m, 15H, CH_{Ar}), 7.63 (s, 1H, CH_{Het}) [c]
14d	NMePh	C_6H_5	1529	3.55 (s, 3H, NCH_3), 7.61 (s, 1H, CH_{Het}), 7.28 – 7.89 (m, 10H, CH_{Ar}) [c]
14e	Morpholino	C_6H_5	1539	3.43–3.47 (m, 4H, NCH_2), 3.71 – 3.74 (m, 4H, OCH_2), 7.74 (s, lH, CH_{Het}), 7.27 – 7.88 (m, 5H, CH_{Ar}) [c]
14f	Pyrrolidino	C_6H_5	1559	1.98 – 2.02 (m, 4H, CH_2), 3.39 – 3.44 (m, 4H, NCH_2), 7.56 (s, 1H, CH_{Het}), 7.26 – 7.88 (m, 5H, CH_{Ar}) [c]
14g	Piperidino	C_6H_5	1545	1.62 (m, 6H, CH_2), 3.47 (m, 4H, NCH_2), 7.65 (s, 1H, CH_{Het}), 7.26 – 7.86 (m, 5H, CH_{Ar})[c]
14h	Me_2N	t-Bu	1561[b]	1.30 (s, 9H, CH_3), 3.08 (s, 6H, NCH_3), 6.61 (s, 1H, CH_{Het})
14i	Et_2N	t-Bu	1548[b]	1.22 (t, 6H, CH_3), 1.25 (s, 9H, CH_3), 3.42 (q, 4H, NCH_2), 6.51 (s, lH, CH_{Het})
14j	Bz_2N	t-Bu	1540[b]	1.30 (s, 9H, CH_3), 4.61 (s, 4H, NCH_2), 6.60 (s, 1H, CH_{Het}); 7.29 – 7.32 (m, 10H, CH_{Ar})
14k	NMePh	t-Bu	1530[b]	1.27 (s, 9H, CH_3), 3.50 (s, 3H; NCH_3), 6.51 (s, 1H; CH_{Het}), 7.18 –7.43 (m, 5H, CH_{Ar})
141	Morpholino	t-Bu	1537[b]	1.23 (s,9H, CH_3), 3.39 – 3.43 (m, 4H, OCH_2), 3.76 – 3.79 (m, 4H, NCH_2), 6.67 (s, 1H, CH_{Het})
14m	Pyrrolidino	t-Bu	1555[b]	1.29 (s, 9H, CH_3), 1.99 – 2.04 (m.4H, CH_2), 3.41 – 3.46 (m, 4H, NCH_2), 6.55 (s, 1H, CH_{Het})
14n	Piperidino	t-Bu	1538	1.27 (s, 9H, CH_3), 1.65 – 1.69 (m, 6H, CH_2), 3.41 – 3.44 (m, 4H, NCH_2), 6.62 (s, 1H, CH_{Het})
14o	Me_2N	Me	1562	2.23 (s, 3H, CH_3), 3.07 (s, 6H, NCH_3), 6.53 (s, 1H, CH_{Het})

Nr.	R_2N	*R*	*IR*, ν_{CN} [cm^{-1}][a)]	*^{1}H-NMR, δ-values, in $CDCl_3$ (assignment)*
14p	Et_2N	Me	1546[b)]	1.23 (t, 6H, CH_3) 2.21 (s, 3H, CH_3), 3.45 (q, 4H, NCH_2), 6.49 (s, 1H, CH_{Het})
14q	Bz_2N	Me	1532	2.26 (s, 3H, CH_3), 4.62 (s, 4H, NCH_2), 6.57 (s. 1H, CH_{Het}), 7.24 – 7.35 (m, 10H, CH_{Ar})
14r	Morpholino	Me	1533	2.21 (s, 3H, CH_3), 3.39 – 3.42 (m, 4H, NCH_2), 3.75 – 3.78 (m, 4H, OCH_2), 6.63 (s, 1H, CH_{Het})
14s	Pyrrodino	Me	1551	2.00 – 204 (m, 4H, CH_2), 2.24 (s, 3H, CH_3), 3.40 – 3.45 (m, 4H, CH_3), 6.49 (s, 1H, CH_{Het})
14t	Piperidino	Me	1534[b)]	1.61 – 1.69 (m, 6H, CH_2), 2.21 (s, 3H, CH_3), 3.40 – 3.45 (m, 4H, NCH_2), 6.55 (s, 1H, CH_{Het})
14u	NMePh	Me	1523	2.23 (s, 3H, CH_3), 3.49 (s, 3H, NCH_3), 6.46 (s, 1H, CH_{Het}), 7.22 – 7.38 (m, 5H, CH_{Ar})
14v	Pyrrolidino	H	1545	1.99 – 2.04 (m, 4H, CH_2), 3.40 – 3.45 (m, 4H, NCH_2), 6.94 (d, 1H, CH_{Het}), 7.17 (d, 1H, CH_{Het})

[a)] measured in KBr. [b)] measured in as capillar film. [c)] measured in [D_6]-DMSO.

Thus, in the IR spectra of the *N,N*-disubstituted 2-amino-selenazoles **14** intense bands at about 1500 cm^{-1} were recorded. These bands can be attributed to the C=N moiety in these compounds **14.** The absence of bands in the typical range of the valence vibration of the carbonyl, OH, and NH moieties documents the successful transformation of the educts into the corresponding products.

In the ^1H NMR spectra of the *N,N*-disubstituted 2-amino-selenazoles **14,** characteristic signals at about 1.00 to 4.60 ppm and 6.00 to 7.90 ppm were found. Whereas the signals in the first range can be attributed to protons at the *N*-linked alkyl or alkylene groups, the signals in the second range can be attributed to protons at C(5) of the selenazoles **14** as well as to protons at their phenyl moieties. It is worth mentioning, that the protons at the C(5) of the thiazole moiety are more strongly shifted to higher fields than the corresponding protons in analogously substituted 2-amino-thiazoles **3**.[7a]

As expected, the *N,N*-disubstituted 2-amino-selenazoles **14** are, similar to their thiophene and thiazole analogous **2** and **3,** highly reactive to different types of electrophilic reagents. For example, with aryl diazonium salts, with reactive formyl derivatives, or with squaric acid deeply coloured products are formed. Whereas some of these results have been reported recently,[21,22] other reports are in preparation.

EXPERIMENTAL

Melting points were determined by means of a Differential Scanning Calorimeter (Mettler, Toledo) using a heating rate of 5 °C/min. The IR spectra were recorded in potassium bromide pellets or as capillar films with a Philips FTIR spectrometer PU and the NMR spectra with a Varian 300 MHz spectrometer Gemini 300 or with a JEOL 200 MHz spectrometer JNM FX 200. The elemental analytical data were determined by means of a LECO analyser CHNS 932.

Preparation of *N,N*-disubstituted cyanamides 18 (General procedure)

Method A

To a mixture of bromine (79.9 g, 0.5 mol) in water (20 mL), a solution of potassium cyanide (32.5 g, 0.5 mol) in water (150 mL) was added under

stirring at 5 to 10°C over a period of 1 h. After changing the colour of the solution from orange to nearly colourless, a mixture of a dialkylamine **6** (0.5 mol) in chloroform (150 mL) was added under stirring at 0 °C, followed by addition of aqueous sodium hydroxide (10 N, 25 mL). Then the organic layer was separated, washed with water for the elimination of excessive inorganic base, dried, and rectified.

Method B

In a solution of a secondary amine (1 mol) and diethyl ether (200 mL), both dried on KOH, a mixture of cyanogene bromide (53 g, 0.5 mol) in dry diethyl ether (250 mL) is added dropwise under stirring at 10 °C. After filtration of the precipitated amine hydrobromide the filtrate is evaporated, and the remaining residue is rectified.

Method C

In an aqueous sodium hydroxide solution (800 mL, 40 %) an aqueous solution of cyanamide (168 g, 50 %, 2 mol) followed by a mixture of an appropriate alkyl chloride (5 mol) and aliquate 336 (12 g) was added under vigorous stirring in such a way that the temperature did not raise higher than 50 – 60 °C. After 5 h the turbid reaction mixture was cooled at 25 °C and diluted with water (1000 mL) and extracted with benzene (1000 mL). The organic layer was separated, dried with sodium sulphate, and concentrated in vacuo at 60 °C. Solid products were isolated by filtration after addition of hexane, liquid products by rectification.

The following *N,N*-disubstituted cyanamides **18** used for the preparation of *N,N*-disubstituted selenoureas **14** were obtained by these methods as follow:

Dimethylaminocyanamid (**18a**), b.p. 52 – 54 °C at 15 Torr (52 °C at 14 Torr[19a]) in a yield of 35 to 40 %, 40 to 45 %, and 25 to 30 % by method A, B, and C, resp.; diethylaminocyanamide (**18b**), b.p. 65 – 67 °C at 10 Torr (68 °C at 10 Torr[19a]) in a yield of 50 to 55 %, 55 to 60 %, and 60 to 65 % by method A, B, and C, resp.; dibenzylaminocyanamide (**18c**), m.p. 54 °C (54 °C[19a]) in a yield of 40 to 45 %, 40 to 45 %, and 60 to 65 % by method A, B, and C, resp.; N-cyan-N-methyl-aniline (**18d**), b.p. 105 –107 at 2 Torr (136 °C at 10 Torr[19a]) in a yield of 65 to 70 % and 60 to 65 % by method A and B, resp.; 4-cyano-morpholine (**18e**), b.p. 85 – 87 °C at 2.5 Torr in a yield of 45 to 50 % and 55 to 60 % by method A and B, resp.; 1-cyanopyrrolidine (**18f**), b.p. 110 – 112 °C at 10 Torr in a yield

of 50 to 55 % by both the methods A and B; 1-cyano-piperidine (**18g**), b.p. 96 – 97 °C at 9 Torr (102 °C at 10 Torr[19a]) in a yield of 40 to 45 % and 45 to 50 % by method A and B, respectively.

Preparation of *N,N*-disubstituted 2-amino-selenoureas 12 (General procedure)

Generation of gaseous hydrogen selenide

Due to the toxicity of hydrogen selenide all the following procedures were performed in an effectively exhausted hood!

To powered aluminium selenide, prepared by heating of an equimolar mixture of aluminium powder and elemental selenium in a closed steel vessel, and placed in a three-necked bottle, aqueous sulphuric acid (7N) was added dropwise to generate a gentile stream of hydrogen selenide.

Addition of hydrogen selenide to *N,N*-disubstituted cyanamides

To a mixture of an appropriate dialkylcyanamide **18** (0.35 mol) in ethanol (50 mL) and aqueous conc. ammonia (50 mL) placed in a three-necked bottle, equipped with a gas inlet, a condenser, and a thermometer, a continuous stream of hydrogen selenide was slowly injected under stirring at 60°C. The end of the reaction was reached after nearly 6 h and was tested by TLC. For isolation of the products, the reaction mixture was filtered and left standing for 12 h at 0 °C. If solid products formed, they were isolated by filtration. Otherwise, the reaction mixture was concentrated in vacuo until the products precipitated. They were recrystallized from toluene or from a mixture of toluene and methanol.

The *N,N*-disubstituted 2-amino-selenoureas **12** so prepared are listed in Table I.

Synthesis of *N,N*-disubstituted 4-aryl-2-amino-selenazoles 14a – 14g

A mixture of phenacyl bromide (10.0 g; 0.05 mol) and a *N,N*-disubstituted selenourea **12** (0.05 mol) in ethanol (100 mL) was refluxed for 40 min. After addition of triethylamine (7 mL) the mixture was continuously refluxed for 10 min and then cooled to room temperature. So far as the selenazoles crystallised, they were isolated by filtration and recrystallized

for purification. Otherwise, the reaction mixture was diluted with water (500 mL) and extracted with diethyl ether (2 × 100 mL). The organic layer was dried and the remaining residue rectified.

Synthesis of *N,N*-disubstituted 2-amino-4-tert-butyl-selenazoles 14h – 14n

In analogy to the previous procedure 1-bromo-3,3-dimethyl-2-butanon (9.0 g; 0.05 mol) and a *N,N*-disubstituted selenourea **12** (0.05 mol) in ethanol (100 mL) was refluxed for 40 min. The reaction mixture was manipulated as before.

Synthesis of *N,N*-disubstituted 2-amino-4-methyl- and 2-amino-4H-selenazoles 14o – 14v

In analogy to the previous procedure 1-chloro-2-propanone (4.6 g; 0.05 mol) or bromoacetaldehyddiethylacetal (9.9 g, 0.05 mol) and a *N,N*-disubstituted selenourea **12** (0.05 mol) in ethanol (100 mL) was refluxed for 40 min. The reaction mixture was manipulated as before.

In Table III the *N,N*-disubstituted 2-amino-selenazoles **4** prepared by these procedures are listed.

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