A Facile Synthesis of *N*-(4-Aryl-1,3-dithiol-2-ylidene)-amides, *N*-(4- or 5-Aryl-1,3-thiaselenol-2-ylidene)-amides, and *N*-(4-Aryl-1,3-diselenol-2-ylidene)-amides[1]

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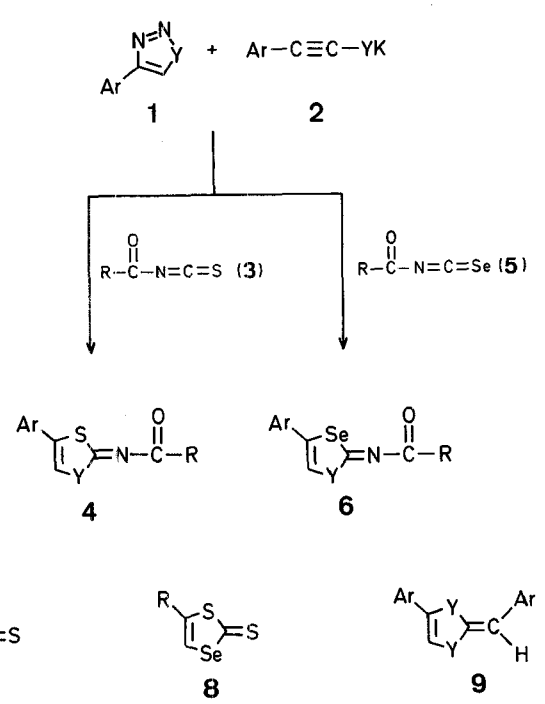
The synthesis of ethyl (4-phenyl-1,3-dithiol-2-ylidene)-carbamate (**4**; Y = S, Ar = C_6H_5, R = OC_2H_5) from the reaction of 4-phenyl-2-thioxo-1,3-dithiole (**7**; Ar = C_6H_5) with either ethyl azidoformate or *N,N*-dichlorourethane in 41 or 10% yield, respectively[2,3] and ethyl (5-substituted 1,3-thiaselenol-2-ylidene)-carbamates (**4**; Y = Se, R = OC_2H_5) from the reaction of 5-substituted 2-thioxo-1,3-thiaselenoles **(8)**[4] with ethyl azidoformate in 30–45% yield[5] has been reported. We describe here a new simple and high yield synthesis of the title compounds.

During our previous work we had observed that 4-aryl-1,2,3-thiadiazoles (**1**; Y = S) and 4-aryl-1,2,3-selenadiazoles (**1**, Y = Se)[6] are unstable in basic medium. In fact with alcoholic solution of potassium hydroxide an immediate effervescene of nitrogen gas occurred and the corresponding fulvenes, namely, *cis*-2, ω-diaryl-1,4-dithiafulvenes (**9**; Y = S) and *cis*-2,ω-diaryl-1,4-diselenafulvenes (**9**; Y = Se) were formed respectively[7,8]. It was shown that potassium arylethynethiolates (**2**; Y = S) and potassium arylethyneselenolates (**2**; Y = Se) are intermediates in these reactions, respectively[7,8,9]. It appeared possible that under certain conditions the bimolecular reaction of **2** leading to the fulvene **9** could be suppressed in favor of cycloaddition of **2** with isothiocyanates **(3)** or isoselenocyanates **(5)**[10]. In fact, reaction of potassium 2-arylethynethiolates (**2**; Y = S) with **3** in tetrahydrofuran gave *N*-(4-aryl-1,3-dithiol-2-ylidene)-amides (**4**; Y = S) and the reaction of **2** (Y = Se) with **3** afforded *N*-(5-aryl-1,3-thiaselenol-2-ylidene)-amides (**4**, Y = Se). Reaction of **2** (Y = S) with **5**, which was prepared *in situ* from the reaction of acetyl or aroyl chloride with potassium selenocyanate in tetrahydrofuran, yielded *N*-(4-aryl-1,3-thiaselenol-2-ylidene)-amides (**6**; Y = S) and the reaction of compound **2** (X = Se) with **5** gave *N*-(4-aryl-1,3-diselenol-2-ylidene)-amides (**6**; Y = Se).



After work up, the products **4** and **6** were sufficiently pure (T.L.C.) in most cases. Where necessary, further purification was achieved by crystallization from acetone or preparative T.L.C. on silica gel. The structure was determined by I.R., N.M.R., and M.S. spectrometry, and in some cases by comparison with an authentic material prepared by known method[2,5].

Melting points were taken on a Kofler hot stage microscope. The I.R. spectra were obtained on a Perkin-Elmer 267 spectrograph. N.M.R. and M.S. spectra were run on a Varian T-60 A and MS-311 spectrometers.

Table 1. *N*-(4-Aryl-1,3-dithiol-2-ylidene)-amides (**4**; X = S) and *N*-(4-Aryl-1,3-thiaselenol-2-ylidene)-amides (**6**; X = S) prepared

Compound No.	Ar	R	Yield [%]	m.p. [°C] (acetone)	Molecular formula[a]	MS *m/e* (M^+)[b]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
4a	C_6H_5	C_6H_5	90	131–133°	$C_{16}H_{11}NOS_2$ (297.4)	297	8.36 (m, $2H_{arom}$); 7.46 (m, $8H_{arom}$); 7.15 (s, 1H, H-4)
4b	C_6H_5	*p*-H_3C—C_6H_4	90	123–125°	$C_{17}H_{13}NOS_2$ (311.4)	311	8.27 (d, $2H_{arom}$); 7.46 (m, $5H_{arom}$); 7.30 (d, $2H_{arom}$); 7.13 (s, 1H, H-4)
4c	C_6H_5	CH_3	60	144–146°	$C_{11}H_9NOS_2$ (235.3)	235	7.34 (m, $5H_{arom}$); 7.10 (s, 1H, H-4); 2.38 (s, 3H, CH_3)
4d	C_6H_5	C_2H_5O	95	124–126°[c]	$C_{12}H_{11}NO_2S_2$ (265.4)	265	7.30 (m, $5H_{arom}$); 7.10 (s, 1H, H-4); 4.33 (q, 2H, OCH_2); 1.40 (t, 3H, CH_3)
4e	*p*-H_3C—C_6H_4	C_6H_5	88	133–135°	$C_{17}H_{13}NOS_2$ (311.4)	311	8.33 (m, $2H_{arom}$); 7.40 (m, $7H_{arom}$); 7.06 (s, 1H, H-4); 2.37 (s, 3H, CH_3)
4f	*p*-H_3C—C_6H_4	*p*-H_3C—C_6H_4	89	131–133°	$C_{18}H_{15}NOS_2$ (325.5)	325	8.40 (d, $2H_{arom}$); 7.43 (d, $2H_{arom}$); 7.23 (dd, $4H_{arom}$); 7.08 (s, 1H, H-4); 2.40 (s, 6H, CH_3)
4g	*p*-H_3C—C_6H_4	CH_3	58	128–130°	$C_{12}H_{11}NOS_2$ (249.4)	249	7.96 (d, $2H_{arom}$); 7.30 (d, $2H_{arom}$); 7.16 (s, 1H, H-4); 2.36 (s, 6H, CH_3)
4h	*p*-H_3C—C_6H_4	C_2H_5O	96	153–154°	$C_{13}H_{13}NO_2S_2$ (279.4)	279	7.53 (d, $2H_{arom}$); 7.23 (d, $2H_{arom}$); 7.10 (s, 1H, H-4); 4.16 (q, 2H, OCH_2); 2.30 (s, 3H, CH_3); 1.33 (t, 3H, CH_3)
4i	*p*-H_3CO—C_6H_4	C_6H_5	90	126–128°	$C_{17}H_{13}NO_2S_2$ (327.4)	327	8.38 (m, $2H_{arom}$); 7.42 (m, $7H_{arom}$); 7.08 (s, 1H, H-4); 3.83 (s, 3H, OCH_3)
4j	*p*-H_3CO—C_6H_4	*p*-H_3C—C_6H_4	85	163–164°	$C_{18}H_{15}NO_2S_2$ (341.5)	341	8.28 (d, $2H_{arom}$); 7.60 (d, $2H_{arom}$); 7.28 (d, $2H_{arom}$); 7.16 (s, 1H, H-4); 6.93 (d, $2H_{arom}$); 3.83 (s, 3H, OCH_3); 2.36 (s, 3H, CH_3)
4k	*p*-H_3CO—C_6H_4	CH_3	55	125–126°	$C_{12}H_{11}NO_2S_2$ (265.4)	265	7.43 (d, $2H_{arom}$); 7.02 (s, 1H, H-4); 6.90 (d, $2H_{arom}$); 3.83 (s, 3H, OCH_3); 2.32 (s, 3H, CH_3)
4l	*p*-H_3CO—C_6H_4	C_2H_5O	95	163–165°	$C_{13}H_{13}NO_3S_2$ (295.4)	295	7.40 (d, $2H_{arom}$); 7.14 (s, 1H, H-4); 6.87 (d, $2H_{arom}$); 4.30 (q, 2H, OCH_2); 3.80 (s, 3H, OCH_3); 1.38 (t, 3H, CH_3)
6a	C_6H_5	C_6H_5	90	136–137°	$C_{16}H_{11}NOSSe$ (344.3)	345	8.40 (m, $2H_{arom}$); 7.50 (m, $8H_{arom}$); 7.16 (s, 1H, H-4)
6b	C_6H_5	*p*-H_3C—C_6H_4	92	141–143°	$C_{17}H_{13}NOSSe$ (3.58.3)	359	8.37 (d, $2H_{arom}$); 7.40 (m, $7H_{arom}$); 7.13 (s, 1H, H-4); 2.33 (s, 3H, CH_3)
6c	C_6H_5	CH_3	65	104–105°	$C_{11}H_9NOSSe$ (282.2)	283	7.46 (m, $5H_{arom}$); 7.13 (s, 1H, H-4); 2.46 (s, 3H, CH_3)
6d	*p*-H_3C—C_6H_4	C_6H_5	85	129–131°	$C_{17}H_{13}NOSSe$ (358.3)	359	8.43 (m, $2H_{arom}$); 7.50 (m, $7H_{arom}$); 7.13 (s, 1H, H-4); 2.40 (s, 3H, CH_3)
6e	*p*-H_3C—C_6H_4	*p*-H_3C—C_6H_4	88	132–134°	$C_{18}H_{15}NOSSe$ (372.4)	373	8.40 (m, $2H_{arom}$); 7.42 (d, $2H_{arom}$); 7.23 (d, $2H_{arom}$); 7.10 (s, 1H, H-4); 6.93 (d, $2H_{arom}$); 2.36 (s, 6H, CH_3)
6f	*p*-H_3CO—C_6H_4	C_6H_5	85	126–127°	$C_{17}H_{13}NO_2SSe$ (374.3)	375	8.43 (m, $2H_{arom}$); 7.33 (m, $7H_{arom}$); 7.10 (s, 1H, H-4); 3.83 (s, 3H, OCH_3)
6g	*p*-H_3CO—C_6H_4	*p*-H_3C—C_6H_4	90	151–153°	$C_{18}H_{15}NO_2SSe$ (388.4)	389	8.23 (d, $2H_{arom}$); 7.20 (m, $6H_{arom}$); 7.10 (s, 1H, H-4); 3.78 (s, 3H, OCH_3); 2.36 (s, 3H, CH_3)

[a] Satisfactory microanalyses obtained: C, ±0.16; H, ±0.21; N, ±0.19

[b] M^+ based on ^{80}Se isotope peak.

[c] Ref.[2], m.p. 122–124°; Ref.[3], m.p. 126°.

N-(4-Aryl-1,3-dithiol-2-ylidene)-amides (4; Y = S); General Procedure:

To a stirred solution of 4-aryl-1,2,3-thiadiazole (**1**, Y = S; 0.01 mol) in dioxan (50 ml), a solution of potassium hydroxide (0.56 g, 0.01 mol) in ethanol (5 ml) is added, whereupon the evolution of nitrogen ceases. The precipitate is filtered, washed with ether, and dissolved in tetrahydrofuran (20 ml). To a stirred solution of the latter at 0 °C is added a solution of substituted isothiocyanate (**3**, 0.01 mol) in tetrahydrofuran (20 ml). Stirring is continued 15 min at 0 °C followed by 15 min at ambient temperature. The solvent is evaporated under reduced pressure, water (50 ml) is added to the residue, and the mixture is extracted with chloroform (2 × 50 ml). The extract is dried with sodium sulfate and filtered. The solvent distilled off, and the residual product purified by crystallization or preparative T.L.C. on silica gel using chloroform/petroleum ether (1:1) as eluent (Table 1).

N-(5-Aryl-1,3-thiaselenol-2-ylidene)-amides (4; Y = Se):

These compounds are prepared from 4-aryl-1,2,3-selenadiazole (**1**; Y = Se) similarly (Table 2).

N-(4-Aryl-1,3-thiaselenol-2-ylidene)-amides (6; Y = S); General Procedure:

To a stirred solution of potassium selenocyanate (1.44 g, 0.01 mol) in tetrahydrofuran (150 ml) at 0 °C, a solution of acetyl or aroyl chloride (0.01 mol) in tetrahydrofuran (10 ml) is added. The stirring

Table 2. *N*-(5-Aryl-1,3-thiaselenol-2-ylidene)-amides (**4**; Y = Se) and *N*-(4-Aryl-1,3-diselenol-2-ylidene)-amides (**6**; Y = Se) prepared

Compound No.	Ar	R	Yield [%]	m.p. [°C] (acetone)	Molecular formula[a]	MS *m/e* (M^+)[b]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
4a	C_6H_5	C_6H_5	92	146–148°	$C_{16}H_{11}NOSSe$ (344.3)	345	8.17 (m, $2H_{arom}$); 7.87 (s, 1H, H-4); 7.50 (m, $8H_{arom}$)
4b	C_6H_5	*p*-H_3C—C_6H_4	87	133–135°	$C_{17}H_{13}NOSSe$ (358.3)	359	8.36 (d, $2H_{arom}$); 7.87 (s, 1H, H-4); 7.47 (m, $7H_{arom}$); 2.41 (s, 3H, CH_3)
4c	C_6H_5	CH_3	55	119–120°	$C_{11}H_9NOSSe$ (282.2)	283	7.67 (s, 1H, H_4); 7.50 (m, $5H_{arom}$); 2.46 (s, 3H, CH_3)
4d	C_6H_5	C_2H_5O	90	141–143°[c]	$C_{12}H_{11}NO_2SSe$ (312.3)	313	7.67 (s, 1H, H-4); 7.33 (m, $5H_{arom}$); 4.33 (q, 2H, OCH_2); 1.40 (t, 3H, CH_3)
4e	*p*-H_3C—C_6H_4	C_6H_5	90	125–127°	$C_{17}H_{13}NOSSe$ (358.3)	359	8.33 (m, $2H_{arom}$); 7.76 (s, 1H, H-4); 7.32 (m, $7H_{arom}$); 2.33 (s, 3H, CH_3)
4f	*p*-H_3C—C_6H_4	*p*-H_3C—C_6H_4	95	136–138°	$C_{18}H_{15}NOSSe$ (372.4)	373	8.33 (d, $2H_{arom}$); 7.77 (s, 1H, H-4); 7.33 (m, $6H_{arom}$); 2.43 (s, 3H, CH_3); 2.40 (s, 3H, CH_3)
4g	*p*-H_3C—C_6H_4	CH_3	50	128–130°	$C_{12}H_{11}NOSSe$ (296.3)	297	7.67 (s, 1H, H-4); 7.33 (q, $4H_{arom}$); 2.44 (s, 3H, CH_3); 2.40 (s, 3H, CH_3)
4h	*p*-H_3C—C_6H_4	C_2H_5O	50	153–155°[d]	$C_{13}H_{13}NO_2SSe$ (326.3)	327	7.67 (s, 1H, H-4); 7.33 (q, $4H_{arom}$); 4.33 (q, 2H, OCH_2); 2.43 (s, 3H, CH_3); 1.40 (t, 3H, CH_3)
4i	*p*-H_3CO—C_6H_4	C_6H_5	85	120–122°	$C_{17}H_{13}NO_2SSe$ (374.3)	375	8.33 (m, $2H_{arom}$); 7.76 (s, 1H, H-4); 7.60 (m, $5H_{arom}$); 7.05 (d, $2H_{arom}$); 3.93 (s, 3H, OCH_3)
4j	*p*-H_3CO—C_6H_4	*p*-H_3C—C_6H_4	90	153–155°	$C_{18}H_{15}NO_2SSe$ (388.4)	389	8.33 (d, $2H_{arom}$); 7.73 (s, 1H, H-4); 7.57 (d, $2H_{arom}$); 7.04 (q, $4H_{arom}$); 3.93 (s, 3H, OCH_3); 2.53 (s, 3H, CH_3)
4k	*p*-H_3CO—C_6H_4	C_2H_5O	50	165–167°[e]	$C_{13}H_{13}NO_3SSe$ (342.3)	343	7.70 (s, 1H, H-4); 7.60 (d, $2H_{arom}$); 7.07 (d, $2H_{arom}$); 4.43 (d, 2H, OCH_2); 3.90 (s, 3H, OCH_3); 1.40 (t, 3H, CH_3)
6a	C_6H_5	C_6H_5	95	124–125°	$C_{16}H_{11}NOSe_2$ (391.2)	393	8.23 (m, $2H_{arom}$); 7.80 (s, 1H, H-4); 7.40 (m, $6H_{arom}$)
6b	C_6H_5	*p*-H_3C—C_6H_4	90	114–115°	$C_{17}H_{13}NOSe_2$ (405.2)	407	8.37 (d, $2H_{arom}$); 7.83 (s, 1H, H-4); 7.63 (m, $7H_{arom}$); 2.43 (s, 3H, CH_3)
6c	C_6H_5	CH_3	52	120–122°	$C_{11}H_9NOSe_2$ (329.1)	331	7.77 (s, 1H, H-4); 7.43 (m, $5H_{arom}$); 2.43 (s, 3H, CH_3)
6d	*p*-H_3C—C_6H_4	C_6H_5	85	143–145°	$C_{17}H_{13}NOSe_2$ (405.2)	407	8.43 (m, $2H_{arom}$); 7.78 (s, 1H, H-4); 7.40 (m, $7H_{arom}$); 2.38 (s, 3H, CH_3)
6e	*p*-H_3C—C_6H_4	*p*-H_3C—C_6H_4	80	138–140°	$C_{18}H_{15}NOSe_2$ (419.3)	421	8.37 (d, $2H_{arom}$); 7.77 (s, 1H, H-4); 7.33 (m, $6H_{arom}$); 2.47 (s, 3H, CH_3); 2.40 (s, 3H, CH_3)
6f	*p*-H_3C—C_6H_4	CH_3	55	122–124°	$C_{12}H_{11}NOSe_2$ (343.2)	345	7.77 (s, 1H, H-4); 7.43 (m, $4H_{arom}$); 2.43 (s, 3H, CH_3); 2.40 (s, 3H, CH_3)
6g	*p*-H_3CO—C_6H_4	C_6H_5	90	133–135°	$C_{17}H_{13}NO_2Se_2$ (421.2)	423	8.50 (m, $2H_{arom}$); 7.77 (s, 1H, H-4); 7.33 (m, $7H_{arom}$); 3.93 (s, 3H, CH_3)
6h	*p*-H_3CO—C_6H_4	*p*-H_3C—C_6H_4	90	140–142°	$C_{18}H_{15}NO_2Se_2$ (435.3)	437	8.28 (d, $2H_{arom}$); 7.73 (s, 1H, H-4); 7.49 (q, $4H_{arom}$); 7.03 (d, $2H_{arom}$); 3.91 (s, 3H, OCH_3); 2.40 (s, 3H, CH_3)

[a] Satisfactory microanalyses obtained: C, ±0.19; H, ±0.18; N, ±0.31.
[b] M^+ based on ^{80}Se isotope peak.
[c] Ref.[5], m.p. 143–144°C.
[d] Ref.[5], m.p. 154–155°C.
[e] Ref.[5], m.p. 166–167°C.

is continued for 15 min. The mixture is added to a stirring solution of potassium arylethynethiolate (**2**, Y = S; 0.01 mol) in tetrahydrofuran (20 ml) at 0°C. Stirring is continued for 15 min at ambient temperature and work up is continued as described in the general procedure for **4** (Y = S) (Table 1).

***N*-(4-Aryl-1,3-diselenol-2-ylidene)-amides (6; Y = Se):**
These compounds are prepared from potassium arylethyneselenolates (**2**; Y = Se) similarly (Table 2).

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