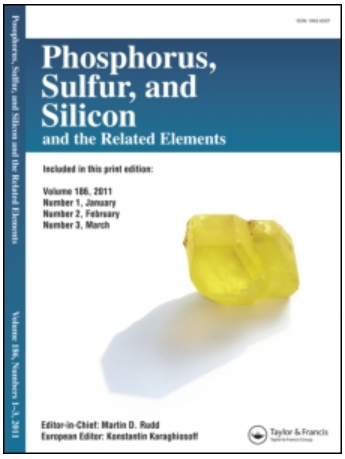


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactions of Thioamides and Selenoamides with Hydrazonoyl Chlorides Under Phase-Transfer Conditions. A Convenient Method of Preparation of δ²-1,3,4-Thiadiazolines and δ²-1,3,4-Selenadiazolines

M. L. Petrov; M. A. Abramov

To cite this Article Petrov, M. L. and Abramov, M. A.(1998) 'Reactions of Thioamides and Selenoamides with Hydrazonoyl Chlorides Under Phase-Transfer Conditions. A Convenient Method of Preparation of δ²-1,3,4-Thiadiazolines and δ²-1,3,4-Selenadiazolines', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 331 — 343
To link to this Article: DOI: 10.1080/10426509808545473
URL: http://dx.doi.org/10.1080/10426509808545473

Phosphorus, Sulfur and Silicon, 1998, 134/135, pp. 331-343
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIONS OF THIOAMIDES AND SELENOAMIDES WITH HYDRAZONOYL CHLORIDES UNDER PHASE-TRANSFER CONDITIONS. A CONVENIENT METHOD OF PREPARATION OF Δ^2-1,3,4-THIADIAZOLINES AND Δ^2-1,3,4-SELENADIAZOLINES

M. L. PETROV* and M. A. ABRAMOV

Department of Organic Chemistry, St. Petersburg State Institute of Technology, Moskovskii pr. 26, 198013 St.-Petersburg, Russia

(Received 26 November, 1997; In final form 13 January, 1998)

Reactions of enolizable thio- and selenoamides with hydrazonoyl chlorides in the presence of bases and phase-transfer catalysts result in 2-dialkylamino-Δ^2-1,3,4-thia- and selenadiazolines. The reactions proceed through formation of corresponding enethiolates and eneselenolates. At 80°C 2-dialkylamino-Δ^2-1,3,4-thia- and selenadiazolines eliminate dialkylamines, giving 2-ylidene-Δ^2-1,3,4-thia- and selenadiazolines in good yield. The reaction of non-enolizable thioamides with hydrazonoyl chlorides in the presence of bases and phase-transfer catalyst occurs as 1,3-dipolar cycloaddition of nitrilimines derived from hydrazonoyl chlorides to the C=S bond, yielding Δ^2-1,3,4-thiadiazolines.

Keywords: Thioamide; selenoamide; thiadiazoline; selenadiazoline; phase-transfer catalysis; hydrazonoyl chloride

INTRODUCTION

It is known that 1,3,4-thiadiazolines can be prepared in the following ways: by reaction of hydrazonoyl chlorides with thiocarbonyl compounds and by cyclization of carbothiohydrazides.

* Corresponding Author. e-mail : halcogen@tu.spb.ru.

As a rule, the first way is 1,3-dipolar cycloaddition of nitrilimines derived from hydrazonoyl chorides to thiocarbonyl compounds[1,2]. Thiones are known to behave in these reactions as superdipolarophiles [3]. However, secondary and teriary thioamides react slowly with nitrilimines: usually, the reaction is complete only in 2–3 days [2]. Reaction of primary thioamides with nitrilimines under similar conditions leads to such linear compounds as thiohydrazides and bis(hydrazonoyl) sulfides[4]. However, reactions of several hydrazonoyl chlorides with primary thioacetamide or thioacetamide-thiobenzamide mixture in boiling toluene afford 2-(thioacetyl)methylene-1,3,4-thiadiazoles in a poor yield[5]. A number of byproducts are formed, among which the same bis(hydrazonoyl) sulfides were found[4,5]. The authors consider 2-ylidene-1,3,4-thiadiazolines as intermediates in these reactions[5]. Also, derivatives of 2-ylidene-1,3,4-thiadiazolines are formed by 1,3-dipolar addition of nitrilimines to labile thioketenes[6], β-keto thio acid anilides[7], and 5-aryl-1,2-dithioles-3-thiones[8].

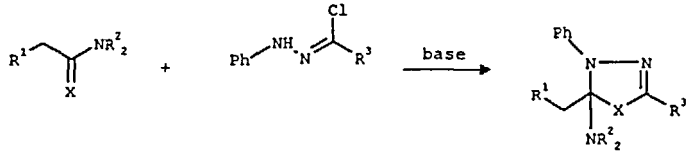
The second way to 1,3,4-thiadiazolines is acylation of carbothiohydrazides. This reaction leads, as a rule, to 1,3,4-thiadizolium salts[9,10]. Treatment of these salts with triethylamine results both in 2-ylidene-1,3,4-thiadizolines and in their dimers[11]. Condensation of 2-methylthio-1,3,4-thiadiazolium salts with such CH acids as $X\text{-}CH_2\text{-}Y$ (X,Y = COOEt; COMe; H and COOEt; $CO(CH_2)_2CO$; H and COMe) yields β,β-disubstituted 2-ylidene-1,3,4-thiadiazolines[12]. Selective deacylation of 2-diacetylylidene-1,3,4-thiadiazolines gives the same heterocycles[12,13]. These compounds are also obtained by direct acylation of N-arylbenzothiohydrazides[14] and are easily interconverted under the action of P_2O_5 or $Hg(OAC)_2$[15].

Recently, we proposed the third way to 1,3,4-thia- and selenadiazolines from α,β-unsaturated thiolates and selenolates and nitrilimines. So, the reaction of 1-dialkylaminoethene thiolates and selenolates with nitrilimines results in 2-dialkylamino-Δ^2-1,3,4-thia- and selenadiazolines[16–19]. Potassium 2-arylethynethiolates and selenolates react with nitrilimines to give 2-ylidene-1,3,4-thia- and selenadiazolines[20–22]. The same compounds were obtained by us from electrochemically generated α,β-unsaturated thiolates and selenolates[23,24]. The structure of 2-dialkylamino-Δ^2-1,3,4-thia- and selenadiazolines thus obtained was confirmed by x-ray analysis [16,25], and their toxicity and radioprotective properties were also studied [26].

In this communication we report a new one-pot synthesis of Δ^2-1,3,4-thia- and selenadiazolines from thio- and selenoamides and hydrazonoyl chlorides in the presence of bases and phase-transfer catalysts. We also made an attempt to estimate limitations and mechanism of this reaction.

RESULTS AND DISCUSSION

We have found that enolizable N,N-dialkylthio- and selenoamides **1a-1n** react with hydrazonoyl chlorides **2a-2e** in the presence of bases, yielding only 2-dialkylamino-Δ^2-1,3,4-thia- and selenadiazolines **3a-3p**.



1a-1n **2a-2e** **3a-3p**

1 (X, R^1, NR^2_2): **a** – S, Ph, piperidino; **b** – S, *p*-$EtOC_6H_4$, morpholino; **c** – S, *p*-MeC_6H_4, morpholino;
d – S, *p*-BrC_6H_4, morpholino; **e** – Se, Ph, NEt_2;
f – Se, Ph, piperidino;
g – Se, Ph, morpholino; **h** – Se, *p*-$EtOC_6H_4$, NEt_2;
i – Se, *p*-MeC_6H_4, NEt_2;
j – Se, *p*-ClC_6H_4, NEt_2; **k** – Se, *p*-$NO_2C_6H_4$, NEt_2;
l – Se, *t*-Bu, NEt_2;
m – Se, H, morpholino; **n** – Se, $R^1 + NR^2_2 = CH_2CH_2NMe$.

2(R^3): **a** – Ph; b – COOEt; **c** – *p*-$NO_2C_6H_4$; **d** – Ac;
e – COPh.

3 (X, R^1, NR^2_2, R^3): **a** – S, Ph, piperidino, Ac; **b** – S, *p*-BrC_6H_4, morpholino, **c** – S, Ph, morfolino, Ac;
d – S, *p*-MeC_6H_4, morpholino, Ac;
e – S, *p*-$EtOC_6H_4$, morpholino, Ac;
f – S, Ph, piperidino, COOEt; **g** – Se, Ph, piperidino, Ac; **h** – Se, *p*-MeC_6H_4, NEt_2, Ac,

i – Se, *p*-ClC_6H_4, NEt_2, Ac; **j** – Se, Ph, morpholino, Ac; **k** – Se, Ph, NEt_2, Ac;

l – Se, Ph, NEt_2, *p*-$NO_2C_6H_4$; **m** – Se, *p*-$EtOC_6H_4$, NEt_2, COOEt; **n** – Se, H, morpholino, Ac;

o – Se, $R^1 + NR^2_2 = CH_2CH_2NMe$, COPh, **p** – Se, $R^1 + NR^2_2 = CH_2CH_2NMe$, *p*-$NO_2C_6H_4$.

In order to optimize the reaction conditions we studied the influence of the nature of the base on the yield of thiadiazoline **3a** and selenadiazoline **3g** in reactions of phenylthioacetic acid piperidide **1a** and phenylselenacetic acid piperidide **1f** with N-phenyl-2-oxopropanohydrazonoyl chloride **2d** (Table I). We have found that the highest yields of the products are obtained when potassium carbonate is used as base, and ammonium salts as phase-transfer catalyst. The yields and properties of products **3a-3p** obtained by reactions of dialkylthio- and dialkylselenoamides **1a-1n** with hydrazonoyl chlorides **2a-2e** in the presence of potassium carbonate and tetrabutylammonium bromide are given in Table II.

TABLE I Influence of base and phase-transfer catalyst on the yield of 1,3,4-thiadiazoline **3a** and 1,3,4-selenadiazoline **3g** (20 °C)

Compound No.	*Base*	*Solvent*	*Yield, %*
3a	40%NaOH/ NBu_4Br	Benzene	44
"	KOH/NBu_4Br	"	53
"	K_2CO_3/18-crown-6	"	75
"	K_2CO_3/ NBu_4Br	"	83
3g	EtOLi	THF	60
"	EtONa	"	72
"	EtOK	"	67
"	*t*-AmONa	Benzene	60
"	40%NaOH/NBu_4Br	"	40
"	KOH/NBu_4Br	"	67
"	K_2CO_3/18-crown-6	"	87
"	K_2CO_3/NBu_4Br	"	93

TABLE II 1,3,4-thiadiazolines and 1,3,4-selenadiazolines **3a-3p**

No.[a]	*Yield, % (mp, °C)*[b]	*IR spectrum, ν, cm⁻¹*		*¹H NMR spectrum (CCl_4), δ, ppm*[c]	*Formula*	*Found (%)/ [Requires]%*
		C=O	*C=N*			
3a	83 (116–118)	1680	1600	1.55 m (6H), 2.15 c (3H), 2.55 m (4H), 3.40 d (1H), 3.60 d (1H)	$C_{22}H_{25}N_3OS$	[a]
3b	87 (153–155)	1670	1600	2.22 s (3H), 2.60 m (4H), 3.75 m (4H), 3.25 d (1H), 3.46 d (1H)	$C_{21}H_{22}BrN_3O_2S$	C 53.40; H 5.37 [C 54.79; H 4.82]
3c	75 (120–124) decomp.	-	-	1.50 m (6H), 2.60 m (4H), 3.47 d (1H), 3.78 d (1H),	[d]	-
3d	85 (118–119)	1670	1600	2,15 s (3H), 2.22 s (3H), 2.60 m (4H), 3.30 d (1H), 3.62 d (1H), 3.75 m (4H)	$C_{22}H_{25}N_3O_2S$	C 66.38; H 6.33 [C 66.81; H 6.37]
3e	82 (145–148)	1675	1600	1.30t (3H), 2.26 s (3H), 2.65 m (4H), 3.28 d (1H), 3.68 d (1H), 3.89 m (4H)	$C_{23}H_{27}N_3O_3S$	C 65.60; H 6.37 [C 64.92, H 6.40]
3f	80 (92–94) decomp.	1710	1600	0.80 t (3H), 1.19 m (6H), 2 31 m (4H), 3.10 d(1H), 3.45 d (1H)	[d]	-
3g	90 (139–140)	1680	1600	1.15 m (6H), 1.90 s (3H), 2.15 m (4H), 3.02 d (1H), 3.74 d (1H)	$C_{22}H_{25}N_3OSe$	[a]
3h	95 (120–121)	1680	1590	0.75 t (6H), 1.87 s (3H), 1.93 s (3H), 2.30 m (4H), 2.98 d (1H), 3.52 d (1H)	$C_{22}H_{27}N_3OSe$	C 61.80; H 6.68 [C 61.59; H 6.57]
3i	81 (115–116)	1720	1605	0.74 t (6H), 0.84 t (3H), 2.34 q (2H), 2.46 q (2H), 2.88 d (1H), 3.58 d (1H), 3.86 q (2H)	$C_{22}H_{26}ClN_3O_2Se$	C 56.52; H 5.48 [C 55.17; H 5.47]

No.[a]	*Yield, % (mp, °C)*[b]	*IR spectrum, ν, cm⁻¹*		*¹H NMR spectrum (CCl_4), δ, ppm*[c]	*Formula*	*Found (%)/ [Requires]%*
		C=O	*C=N*			
3j	90 (146–148)	1670	1605	2.02 s (3H), 2,18 m (4H), 3.08 d (1H), 3.48 m (4H+1H)	$C_{21}H_{23}N_3O_2Se$	C 58.83 ; H 5.85 [C 58.88; H 5.41]
3k	93 (105–110)	1680	1600	0.74 t (6H), 1.94 s (3H), 2.40 m (4H), 2.94 d (1H), 3.68 d (1H)	$C_{21}H_{25}N_3OSe$	C 62.20; H 6.13 [C 60.87; H 6.08]
3l	90 (114–115)	1320[e]	1620	0.70 t (6H), 2.22 q (2H), 2.55 q (2H), 2.98 d (1H), 3.70 d (1H)	$C_{25}H_{28}N_4O_2Se$	C 60.90; H 5.51 [C 60.85; H 5.31]
3m	60 (decomp)	1720	1605	1.02 t(6H), 1.36 m(6H), 2.70 m (5H), 3.88 m (3H), 4.18 q (2H)	$C_{24}H_{31}N_3O_3Se$	-
3n	85 (125–127)	1680	1600	2.01 s (3H), 2.40 s (3H), 2.45 m (4H), 3.70 t (4H)	$C_{15}H_{19}N_3O_2Se$	C 51.34; H 5.61 [C 51.14; H 5.44]
3o	72 (81–83)	1645	1600	1.15 m (2H), 1.88 s (3H), 2.35 m (4H)	$C_{18}H_{19}N_3OSe$	C 58.19; H 6.23 [C 58.07; H 5.14]
3p	70 (133–134)	1340[e]	1615	1.25 m (2H), 1.87 s (3H), 2.40 m (4H)	$C_{18}H_{18}N_4O_2Se$	C 54.10; H 4.61 [C 53.87; H 4.52]
3q	60 (123–125)	1345[e] 1665	1590	2.03 s (6H), 2,15 s (3H)	$C_{18}H_{18}N_4O_3S$	C 58.14; H 4.82 [C 58.36; H 4.90]

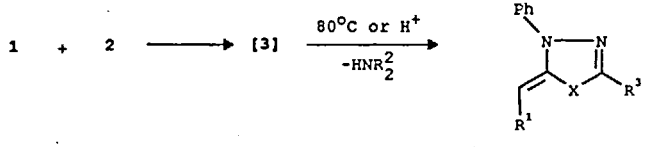
Notes : [a] Compounds **3a** and **3g** were described in [16] and [25], respectively. [b]Compounds **3c**, **3e** were recrystallized from heptane, **3b** from benzene-heptane, **3a** from pentane, and compounds **3d**, **3f**, **3g-3p** from hexane. [c]Non-aromatic protons only. [d] The compound is stable only in solution at low temperature. [e] $\nu_{N\text{-}O}$.

The reaction under study has the following limitations. First, steric hindrance created by the diisopropylamino group in thio- and selenoamides **1** prevents them from reacting with hydrazonoyl chlorides **2**. Second, products **3c** and **3f** are very unstable, and they can be detected only in solution. On the other hand, compounds **3o** and **3p** resulting from reactions of N-methylpyrrolidine-2-selone **1n** with hydrazonoyl chlorides **2c** and **2e**, despite spirocyclic structure, are fairly stable.

The ^{1}H NMR spectra of compounds **3** contain signals at δ 2.88–3.28 ppm, d (1H), and 3.43–3.78 ppm, d (1H), as an *AB* system with a spin-spin coupling constant *J* of 14–16.3 Hz. These signals could be assigned to hydrogen atoms of the methylene group of *p*-R-benzyl substitutents at the 5-position of Δ^2-1,3,4-thia- and selenadiazolines **3** ring. In the spectra of compounds **3a-3p** we also observed the expected proton signals from other substituents. The IR spectra of heterocyclic compounds **3a-3p** contain absorption bands of C=N bond of the heterocycle at 1590–1620 cm^{-1}. In spectra of compounds containing a carbonyl group, carbonyl absorption bands at 1645–1720 cm^{-1} are present. As a whole, the ^{1}H NMR and IR spectra given in Table II are similar to those of heterocycles **3a** and **3g**, whose stucture was confirmed previously by x-ray analysis [16,25].

Δ^2-1,3,4-Thia- and selenadiazolines **3** are almost colorless crystalline compounds, which are fairly stable as crystals and in inert solvents. They easily loose a molecule of dialkylamine with rise in temperature or under the action of acids, thus being converted into 5-ylidene-Δ^2-1,3,4-thia- and selenadiazolines **4a-4l.** When the reactions of thio- or selenoamide **1** with hydrazonoyl chlorides **2** were carried at 80°C, the products were only compounds **4**.

Products **4** are strongly colored (from yellow to violet) stable crystalline compounds; their yields and spectral properties are given in Table III. The ^{1}H NMR and IR spectra of **4** resemble those of Δ^2-1,3,4-selenadiazole **4d**, whose structure was proved by x-ray analysis [22]. Some compounds were obtained previously by other methods[11,17,21,22].



4a-4l

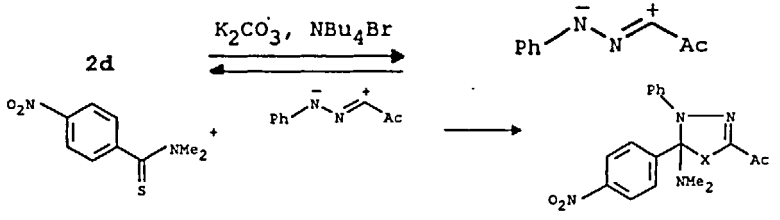
TABLE III 1,3,4-thiadiazilines and 1,3,4-selenadiazolines **4a-4l**

No.[a]	*Yield, % (mp, °C)*[b]	*IR spectrum, ν, cm⁻¹*		*¹H NMR spectrum (CCl_4), δ, ppm*[c]	*Formula*	*Found (%)/ [Requires]%*
		C=O	*C=N*			
4a	82 (123–125)	1720	1585	0.80 t (3H), 4.25 q(2H), 5.90 s (1H)	$C_{18}H_{16}N_2O_2S$	[a]
4b	85 (120–121)	-	1596	6.00 s (1H)	$C_{21}H_{16}N_2S$	[a]
4c	86 (144–145)	1666	1584	2.40 s (3H), 6.00 s (1H)	$C_{17}H_{14}N_2OS$	[a]
4d	90 (100–101)	1720	1575	1.34 t (3H), 1.36 t(3H), 3.96 q (2H), 4.33 q (2H), 6.05 s (1H)	$C_{20}H_{20}N_3O_2Se$	[a]
4e	57 (123–125)	1780	1585	1.21t (3H), 4.24 q (2H), 6.01 s (1H)	$C_{16}H_{18}N_2O_2Se$	C 56.51; H 4.22 [C 56.82, H 4.50]
4f	78 (118–119)	1720	1575	1.20 t (3H), 2.16 s (3H), 4.24 q (2H), 6.01 s(1H)	$C_{19}H_{18}N_2O_2Se$	C 59.12; H 4.60 [C 59.26; H 4.71]
4g	62 (136–137)	1730	1575	1.22 t (3H), 4.25 q (2H), 5.98 s (1H)	$C_{18}H_{15}ClN_2O_2Se$	C 53.80; H 3.75 [C 53.25; H 3.69]
4h	25 (208–209)	1700	1595	1.30 t (3H), 4.33 q (2H), 6.05 s (1H)	$C_{18}H_{15}N_3O_4Se$	C 52.36; H 3.50 [C 51.95; H 3.63]
4i	65 (114–115)	-	1590	6.25 s (1H)	$C_{21}H_{16}N_2Se$	C 67.70; H 4.18 [C 67.20; H 4.30]
4j	90 (214–216)	-	1590	6.26 s (1H)	$C_{21}H_{15}N_3O_2Se$	C 61.24; H 3.96 [C 60.01; H 3.60]
4k	86 (144–145)	1675	1580	2.43 s (3H), 6.05 s (1H)	$C_{17}H_{14}N_2OSe$	C 59.40; H 4.71 [C 54.70; H 5.74]
4l	60 (oil)	-	-	1.00 s (9H), 1.26 t (3H), 4.28 q (2H), 9.01 s (1H)	[d]	-

Notes : [a] Compounds **4a,4c** were described in [21], **4b** in [11,21], **4d** in [17,22] respectively. [b] From ethanol. [c] Non-aromatic protons only. [d] The compound is stable only in solution at low temperature.

4 (X, R^1, R^3): **a** – S, Ph, COOEt; **b** – S, Ph, Ph; **c**- S, Ph, Ac; **d** – Se, *p*-$EtOC_6H_4$, COOEt; **e** – Se, Ph, COOEt; **f** – Se, *p*-MeC_6H_4, COOEt; **g** – Se, *p*-ClC_6H_4, COOEt; **h** – Se, *p*-$NO_2C_6H_4$, COOEt; **i** – Se, Ph, Ph; **j** – Se, Ph, *p*-$NO_2C_6H_4$; **k** – Se, Ph, Ac; **l** – Se, *t*-Bu, COOEt.

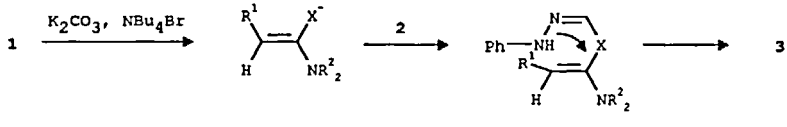
The reaction of non-enolizable N,N-dimethyl-*p*-nitrothiobenzamide **1o** with phenylhydrazonoyl chloride **2d** in the presence of potassium carbonate and tetrabutylammonium bromide occurs as 1,3-dipolar cycloaddition of nitrilimine, derived from the hydrazonoyl chloride, across the C=S bond of the thioamide to yield Δ^2-1,3,4-thiadiazolines and is complete in 2–3 days.



1o **3q**

In a similar way, reactions of enolizable thio- and selenoamides **1** with nitrilimines in the presence of such a weak base as triethylamine, which is usualy used for preparation of nitrilimines, proceeds very slowly and is complete only in 2–3 days. When the reaction is carried out under conditions of phase-transfer catalysis, it takes only 10–15 min to attain the same yield of the product.

We presume that the reaction of enolizable thio- and selenoamides **1** with hydrazonoyl chlorides **2** in the presence of a phase-transfer catalyst begins with formation of ethenethiolate and selenolate intermediates which then attack the electrophilic center of the hydrazonoyl chloride and replace the halogen in it. The subsequent intramolecular cyclization of intermediate linear product results in the corresponding Δ^2-1,3,4-thia- and selenadiazolines **3**.



The proposed mechanism is confirmed by the influence of β-substituents in etheneselenolates on the reaction with hydrazonoyl chlorides **2**, which was studied by the method of competing reactions of hydrazonoyl chloride **2b** with lithium 1-diethylamino-2-*p*-R-phenyletheneselenolates in benzene. Lithium etheneselenolates were prepared from the corresponding selenoamides **1e,1h-1k** (R = H, EtO, Me, Cl, NO_2, respectively). The ratio of products in the reaction mixtures was determined by HPLC. It was found that electron-donor substituents favor the reaction and increase the nucleophilicity of the selenolate. Electron-acceptor substituents slow down the reaction. The same products (compounds **3**) are formed when the reaction is carried out in the presence of such a weak base as triethylamine, but in this case the effect of substituents in the diethylselenoamides **1e,1h-k** is the opposite, as was established by the method of competing reactions: electron-acceptor substituents accelerate the reaction. The data obtained can be explained on the assumption that selenadiazolines are formed by reaction of etheneselenolates with hydrazonoyl chloride and that the rate-determining stage is deprotonation of the selenamide by triethylamine. This assumption also explains the strongly reduced rate of the formation of selenadiazolines from selenoamides, whereas the reaction of preliminarily prepared etheneselenolates with nitrilimines proceeds almost instantly.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Tesla BS-487C spectrometer at 80 MHz with HMDS as internal standart. The IR spectra were recorded on an IKS-29 spectrophotometer in KBr. The progress of reactions and purity of products were monitored by TLC on Silufol UV-254 plates, development with iodine vapor or UV light.

The product ratio in the competing reactions was determined by HPLC on a Laboratorni Pristroje liquid chromatograph (Czech) (UV detector, wavelength 254 nm) equipped with Separon SGX C18 columns (250 × 4 mm), using ethanol-water or acetonitrile-water mixtures as eluents.

N,N-Diakylthioamides and N,N-dialkylselenoamides **1a-1n** were obtained from the corresponding 4-substituted 1,2.3-thia- and selenadiazoles and secondary amines in the presence of potassium hydroxide [27]. N-Methylpyrrolidine-2-selone **1n** was obtained by the method reported in [28].

2-Dialkylamino-Δ^2-1,3,4-thia- and -selenadiazolines 3 and 5-ylidene-Δ^2-1,3,4-thia- and selenadiazolines 4
(the reaction conditions are given in Table I)

a. To a solution of 2.5 mmol of alcohol in 10 mL of solvent 3 mmol of metallic sodium or lithium (prepared as thin plates) or of metallic potassium were added, and the mixture was refluxed for 8 h until the liberation of hydrogen had ceased. When the reaction was complete, the resulting mixture was allowed to cool to room temperature and 2.5 mmol of dialkylamide **1** in 5 mL of benzene (distilled over sodium) were added dropwise with vigorous stirring. The mixture was stirred for 30 min, and a solution of 2.5 mmol of phenylhydrazonoyl chloride **2d** in the same solvent was added dropwise. The reaction mixture was stirred for 40 min and filterred, and the mother liquor was evaporated under reduced pressure. The residue was crystallized by grinding with 10–15 ml of cold ethanol. The resulting light-yellow powder was filtered off and washed with ethanol and pentane. After crystallization from appropriate solvent, pure compound **3a** or **3g** was obtained. When the residue obtained after evaporation of the solvent was dissolved in 25 mL of benzene and filterred through a layer of silica gel, pure 5-ylidene-Δ^2-1,3,4-thia- and selenadiazolines **4c, 4k** were isolated by removal of the solvent under reduced pressure. 5-Ylidene-Δ^2-1,3,4-thia- and selenadiazolines **4c, 4k** were also formed on recrystallization of 2-dialkylamino-Δ^2-1,3,4-thia- and selenadiazolines **3a, 3g** from ethanol.

b. To a solution of 2.5 mmol of N,N-dialkylamide **1** and 0.2 g of the phase-transfer catalyst in 5 mL of benzene 1.0 g of a base as a fine power or a concentrated solution was added. A solution of 2.55 mol of phenylhydrazonoyl chloride **2** in 5 mL of benzene was added dropwise over a period of 30 min with vigorous stirring at room temperature. The end of the reaction was determined by the disappearance of the initial amide **1** according to TLC. The reaction mixture was filterred, and the mother liquor was evaporated under reduced pressure. The residue was crystallized by grinding with 10–15 mL of ethanol. The resulting suspension was cooled to 0°C, and the light yellow powder was filtered off, washed with 5 ml of cold ethanol and then with pentane, and recrystallized from hexane. In Tables II, III the yields of compound **3** and **4** are given for the case, when NBu_4Br as the catalyst and K_2CO_3 as the base were used.

Reactivity of lithium l-diethylamino-2-arylетheneselenolates

The study was performed with the reaction of N,N-diethylselenoamides **1a, d-g** with phenylhydrazonyl chloride **2d** in the presence of lithium diisopropylamide. The ratio of the products was determined by HPLC with a 95:25 acetonitrile-water mixture as eluent (1 mL/min). A solution of lithium diisopropylamide was prepared from 2 mL of tetrahydrofuran, 1 mL of a 1 N solution of butyllithium in hexane, and 0.17 mL of diisopropylamine in a dropping funnel. To a solution of 0.5 mmol of N,N-diethylphenylselenoamide and 0.5 mmol of N,N-diethyl-*p*-R-phenylselenoamide in 3 mL of tetrahydrofuran, maintained at −78°C, a solution of lithium diisopropylamide was added dropwise, and the mixture was stirred for 20 min. A solution of 0.1 mmol of phenylhydrazonoyl chloride **2d** and 0.2 mmol of triethylamine in 1 mL of THF was then added in one portion, and the mixture was stirred for 20 min. The reaction mixture was kept for 1 h and then allowed to warm up to room temperature. The solution was evaporated under reduced pressure, and the residue was dissolved in 10 mL of benzene. The resulting solution was passed through a layer of silica gel L 40/100 (5 cm^3). The mother liquor was evaporated to dryness. A 5–10-mg portion of the residue was dissolved in 1 mL of THF, and 2–5-μL samples were withdrawn. The products were identified by adding authentic compounds to the sample. Quantitative compositions of the mixtures were calculated by the external standard method. The following relative rate constants were obtained: $k_{rel} = 0.021 - 0.956\delta^0_p$, r = 0.998, s = 0,10.

Compound No.	**1e**	**1h**	**1g**	**1i**	**1k**
k_{rel}	1.00	1.47	1.32	0.61	0.17

Study of the reactivity of N-N-diethylselenoamides 1 by the method of competing reactions

To a solution of 0.5 mmol of N,N-diethylphenylselenoamide, 0.5 mmol of N,N-diethyl-*p*-R-phenylselenoamide, and 0.1 mmol of phenylhydrazonoyl chloride **2d** in 2 mL of benzene 0.07 mL of triethylamine was added. The mixture was stirred and was kept for 72 h at 25°C. The ratio of the products was determined by HPLC according to the above procedure. The following relative rate constants were obtained:

Compound No.	**1e**	**1h**	**1g**	**1i**	**1k**
k_{rel}	1.00	0.85	1.23	1.31	4.78.

References

[1] R. Huisgen, R. Grashey, M. Seidel, H. Knupfer, and R. Schmidt, *Liebigs Ann. Chem.* 169 (1962).

[2] P. Wolkoff, S. Hammerum, *Acta Chem. Scand.* **B 30**, 837 (1976).

[3] R. Huisgen and E. Langhals, *Tetrahedron Lett.* **39**, 5369 (1989).

[4] P. Wolkoff and S. Hammerun, *Acta Chem. Scand.* **B30**, 831 (1976).

[5] T. Benincori, E. Brenna, F. Sannicolo, L. Trimarco, and T. Pilati, *Gazz. Chim. Ital.* **123**, 531 (1993).

[6] K. Dickore and R. Wegler, *Angew. Chem. Int. Ed. Engl.* **5**, 970 (1966).

[7] D. Pocar, L. M. Rossi, and P. Trimaica, *J. Heterocyclic Chem.* **12**, 401 (1975).

[8] M. Magnet, G. Poirier, and J. Teste, *Bull. Soc. Chim. Fr.* 1503 (1970).

[9] G. V. Boyd and A. J. H. Summers, *J. Chem. Soc. C*, 2311 (1971).

[10] H. Mastalerz and M. S. Gibson, *J. Chem. Soc. Perkin Trans. 1*, 245 (1983).

[11] T. Mohammad and M. S. Gibson, *Phosphorus, Sulfur, and Silicon*, **70**, 243, (1992).

[12] H. Mastalerz, T. Mohammad, and M. S: Gibson, *Can. J. Chem.* **65**, 2713 (1987).

[13] N. Pandya, A. J. Busile, A. K. Gupta, P. Hand, C. L. MacLaurin, T. Mohammad, S. Ratemi, M. S. Gibson, and M. F. Richardson, *Can. J. Chem.* **71**, 561 (1993).

[14] P. D. Callaghan, J. Elliott, S. S. Gandhy, M. S. Gibson, H. Matalenz, and D. J. Vukov, *J. Chem. Soc. Perkin Trans. 1*, 2948 (1981).

[15] H. Mastalerz and M. S. Gibson, *J. Chem. Soc. Perkin Trans. 1*, 2952 (1981).

[16] M. A. Abramov, M. L. Petrov, M. N. Dzhafarov, A. S. Batsanov, K. A. Potekhin, and Yu. T. Struchkov, *Zh. Obshch. Khim.* **64**, 2018 (1994).

[17] M. L. Petrov, M. A. Abramov, K. A. Potekhin, Yu. T. Struchkov, and A. A. Petrov, *Zh. Org.. Khim.* **26**, 2449 (1990).

[18] M. L. Petrov, M. A. Abramov, V. A. Galishev, M. N. Dzhafarov, A. S. Batsanov, K. A. Potekhin, Yu. T. Struchkov, and A. A. Petrov, *Zh. Org. Khim.* **27**, 1799 (1991).

[19] M. A. Abramov, V. A. Galishev, and M. L. Petrov, *Zh. Org. Khim.* **29**, 2174 (1993).

[20] M. L. Petrov, N. A. Terent'eva, K. A. Potekhin, Yu. T. Struchkov, V. N. Chistokletov, V. A. Galisev, and A. A. Petrov, *Zh. Org. Khim.* **27**, 1573 (1991).

[21] N. A. Terent'eva, M. L. Petrov, K. A. Potekhin, Yu. T. Struchkov, and V. A. Galisev, *Zh. Org. Khim.* **30**, 344 (1994).

[22] N. A. Terent'eva, M. L. Petrov, K. A. Potekhin, V. A. Galishev, and Yu. T. Struchkov, *Zh. Org. Khim.* **30**, 1471 (1994).

[23] M. A. Abramov, M. E. Niyazymbetov, and M. L. Petrov, *Zh. Obshch. Khim.* **62**, 1914 (1992).

[24] M. A. Abramov, M. E. Niyazymbetov, and M. L. Petrov, *Zh. Obshch. Khim.* **62**, 2138 (1992).

[25] M. L. Petrov, M. A. Abramov, K. A. Potekhin, Yu. T. Struchkov, V. A. Galishev, and A. A. Petrov, *Zh. Strukt. Khim.* **180**, 2018 (1992).

[26] L. L. Petrova, L. V. Trufanova, M. L. Petrov, M. A. Abramov, N. I. Zmitrovich, and N. A. Terent'eva, *Khim.-Farm. Zh.* No. 2, 19, (1994).

[27] F. Malek-Yardi and M. Yalpani, *Synthesis*, 328 (1977).

[28] J. P. Michael, W. H. Reid, B. G. Rose, and R. A. Speirs, *Chem. Commun.* 1494, (1988).