

Hamdi M. Hassaneen, Abdelfattah Shetta and Ahmad S. Shawali (1)

Department of Chemistry, Faculty of Science, University of Cairo, Giza Egypt

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Reaction of hydrazidoyl halides **1-5** with potassium selenocyanate in ethanol produces the corresponding 2,4-disubstituted-5-imino- Δ^2 -1,3,4-selenadiazolines, **9-13** respectively. Nitrosation of the latter yields the *N*-nitroso derivatives **14-17**, which decompose upon refluxing in xylene to give 2,4-disubstituted Δ^2 -1,3,4-selenadiazolin-5-ones in good yield. Compounds **9-13** give the respective *N*-acetyl derivatives **22-26** and *N*-benzoyl derivatives **27-31** with acetic anhydride and benzoyl chloride in pyridine.

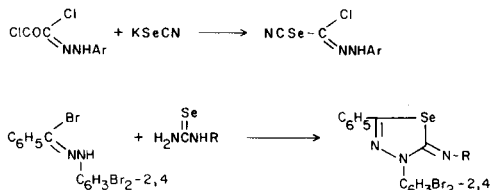
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Hydrazidoyl halides of type **1-6** have been extensively used in synthesis of various nitrogen, oxygen and sulfur heterocyclic compounds (**2-9**). However, little attention has been given to the synthesis of selenium heterocycles from such halides (10,11). In addition, the reaction of hydrazidoyl chlorides **6** with potassium selenocyanate was reported (12) to give substitution on the carboxylic acid chloride function (Scheme 1). This observation was thought to be due to the deactivation of the halo group attached to the C=N group by the neighbouring carbonyl group (2). In an attempt to examine the potentiality of hydrazidoyl halides in synthesis of selenium heterocycles and the effect of the presence of a carbonyl group conjugated with the hydrazone group, we have investigated the reactions of **1-5** with potassium selenocyanate. The results are summarized in Schemes 2 and 3.



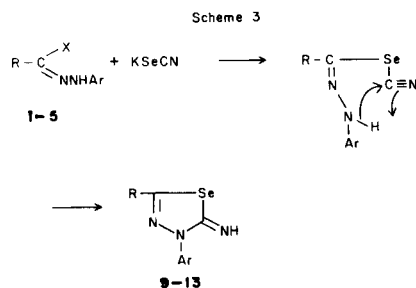
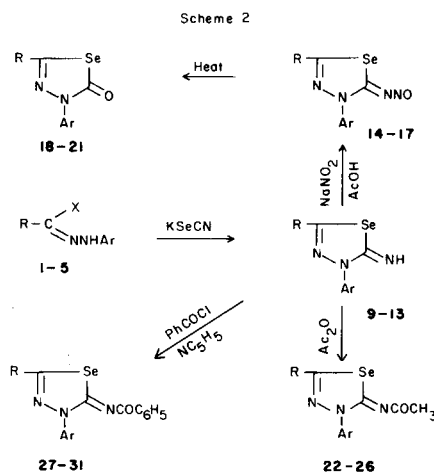
- 1 R = C₆H₅, X = Br
 2 R = CH₃CO, X = Cl
 3 R = C₆H₅CO, X = Br
 4 R = EtOCO, X = Cl
 5 R = C₆H₅NHCO, X = Cl
 6 R = COCl, X = Cl

Scheme 1



Results and Discussion.

Treatment of hydrazidoyl halides **1-5** with potassium selenocyanate in ethanol at room temperature gives in each case the corresponding 5-imino-2,4-disubstituted Δ^2 -1,3,4-selenadiazolines **9-13**, respectively. The structures of the latter products were deduced from their spectral and analytical data together with their chemical reactions described below (Scheme 2). Thus, infrared spectra



of **9-13** show no absorption in the 2050-2150 cm⁻¹ region due to a free SeCN group (13). The spectra revealed, however, bands assignable to imino group near 3300 cm⁻¹. The electronic absorption patterns of the products **9-13** are similar to those reported for their thia analogs (6). The data are summarized in Table 3. The probable reaction sequence leading to **9-13** from **1-5** and potassium selenocyanate is shown in Scheme 3.

Nitrosation of **9-13** yields the corresponding *N*-nitroso derivatives **14-17**, respectively. The latter products exhibit *n*- π^* and π - π^* transition maxima characteristic of the nitrosoimino group near 470 nm (log ϵ < 3) and 284 nm (log ϵ > 4), respectively (14). The infrared spectra of **14-17** were free of NH bands.

Upon refluxing in xylene, all compounds in series **14-17** decomposed and gave the corresponding 2,4-disubstituted

Δ^2 -1,3,4-selenadiazolin-5-ones **18-21**, respectively, in almost quantitative yields. The infrared spectra of the latter products showed, in each case, a strong CO band near 1700 cm^{-1} in addition to other carbonyl bands present in **14-17**. Representative electronic absorption data of **18-21** are given in Table 3.

Acylation of **9-13** with acetic anhydride (and with benzoyl chloride in pyridine) yields the corresponding *N*-acetyl (and *N*-benzoyl) derivatives, respectively (Table 3). Both elemental and spectral data were consistent with the acylated products obtained. The pmr spectra of the acetylated products revealed acetyl proton signal near 2.6 ppm.

The foregoing results indicate that both potassium selenocyanate and potassium thiocyanate behave similarly towards hydrazidoyl halides **1-5**.

EXPERIMENTAL

Melting points are uncorrected. Ir spectra (potassium bromide) were recorded on a Unicam ir spectrophotometer SP1000 spectrophotometer. Uv spectra (ethanol) were determined on a Unicam SP8000 spectrophotometer. ^1H nmr spectra (deuteriochloroform) were recorded with a Varian T60-A spectrometer. Hydrazidoyl halides **1-5** were prepared as previously described (4,15,16).

2,4-Disubstituted-5-imino- Δ^2 -1,3,4-selenadiazolines (**9-13**).

General.

To a suspension of the appropriate hydrazidoyl halide (0.005 mole) in ethanol (50 ml.), potassium selenocyanate (0.01 mole) in water (7 ml.) was added and the mixture was stirred for 2 hours. The mixture was then diluted with water and solid formed was collected, washed with water and finally crystallized from methanol. The products obtained together with physical constants are given in Table 1.

Nitrosation of **9-13**.

A solution of the appropriate imino compound in glacial acetic acid (20 ml.) was treated with an equivalent quantity of sodium nitrite while stirring for 10 minutes. The reddish product which precipitated was collected, washed with water and crystallized from ethanol. The nitroso-imino products **14-17** prepared are given in Table 1.

Thermolysis of **14-17**.

The appropriate *N*-nitrosoimino compound (0.2 g.) was refluxed in xylene (20 ml.) for 25 minutes. The solvent was then evaporated and the residue was triturated with little of petroleum ether (40/60°). The solid formed was collected and crystallized from methanol. The products **18-21** obtained in 85-95% yield are given in Table 1.

Acylation of **9-13**.

The appropriate imino compound **9-13** (1 g.) was refluxed in acetic anhydride (20 ml.) for 20 minutes, cooled and poured on crushed ice. The crude solid which precipitated was collected and crystallized from ethanol.

Table 1

5-Imino-2,4-disubstituted- Δ^2 -1,3,4-selenadiazolines **9-13**

Compound No.	R	Ar	M.p. °C	Molecular Formula	Se % Found	Calcd.
9	C_6H_5	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	210	$\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_2\text{Se}$	22.71	22.86
10a	CH_3CO	C_6H_5	42	$\text{C}_{10}\text{H}_8\text{N}_3\text{OSe}$	29.31	29.67
10b	CH_3CO	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	51	$\text{C}_{11}\text{H}_{11}\text{N}_3\text{OSe}$	27.90	28.18
11a	$\text{C}_6\text{H}_5\text{CO}$	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	102	$\text{C}_{16}\text{H}_{13}\text{N}_3\text{OSe}$	22.88	23.07
11b	<i>p</i> - $\text{MeC}_6\text{H}_4\text{CO}$	C_6H_5	126	$\text{C}_{16}\text{H}_{13}\text{N}_3\text{OSe}$	22.97	23.07
12a	$\text{C}_2\text{H}_5\text{OCO}$	C_6H_5	87	$\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2\text{Se}$	26.45	26.66
12b	$\text{C}_2\text{H}_5\text{OCO}$	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	199	$\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2\text{Se}$	25.53	25.67
12c	$\text{C}_2\text{H}_5\text{OCO}$	<i>p</i> - ClC_6H_4	135	$\text{C}_{11}\text{H}_{10}\text{ClN}_3\text{O}_2\text{Se}$	23.71	23.88
13a	$\text{C}_6\text{H}_5\text{NHCO}$	<i>p</i> - ClC_6H_4	165	$\text{C}_{15}\text{H}_{11}\text{N}_4\text{ClOSe}$	20.80	20.91
13b	$\text{C}_6\text{H}_5\text{NHCO}$	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	177	$\text{C}_{16}\text{H}_{14}\text{N}_2\text{OSe}$	22.12	22.36

5-*N*-Nitrosoimino-2,4-disubstituted- Δ^2 -1,3,4-selenadiazolines **14-17**

14	C_6H_5	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	177	$\text{C}_{14}\text{H}_9\text{N}_5\text{O}_3\text{Se}$	21.41	21.11
15a	CH_3CO	C_6H_5	105	$\text{C}_{10}\text{H}_8\text{N}_4\text{O}_2\text{Se}$	26.54	26.75
15b	CH_3CO	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	171	$\text{C}_{11}\text{H}_{10}\text{N}_4\text{O}_2\text{Se}$	25.30	25.54
16a	$\text{C}_6\text{H}_5\text{CO}$	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	127	$\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2\text{Se}$	20.99	21.12
16b	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CO}$	C_6H_5	128	$\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2\text{Se}$	21.40	21.12
17	$\text{C}_2\text{H}_5\text{OCO}$	C_6H_5	117	$\text{C}_{11}\text{H}_{10}\text{N}_4\text{O}_3\text{Se}$	24.10	24.28

2,4-Disubstituted- Δ^2 -1,3,4-selenadiazolin-5-ones **18-21**

18	C_6H_5	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	170	$\text{C}_{14}\text{H}_9\text{N}_3\text{O}_3\text{Se}$	22.61	22.81
19a	CH_3CO	C_6H_5	77	$\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{Se}$	29.32	29.56
19b	CH_3CO	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	63	$\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2\text{Se}$	28.10	28.08
20a	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CO}$	C_6H_5	75	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{Se}$	23.21	23.00
20b	$\text{C}_6\text{H}_5\text{CO}$	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	139	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{Se}$	22.98	23.00
21	$\text{C}_2\text{H}_5\text{OCO}$	C_6H_5	80	$\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_3\text{Se}$	26.50	26.57

Table 2

Compound No.	R	Ar	M.p. °C	Molecular Formula	Se % Found	Calcd.
5- <i>N</i> -Acetylimino-2,4-disubstituted- Δ^2 -1,3,4-selenadiazolines 22-26						
22	C ₆ H ₅	<i>p</i> -NO ₂ C ₆ H ₄	224	C ₁₆ H ₁₂ N ₄ O ₃ Se	20.21	20.39
23a	CH ₃ CO	C ₆ H ₅	107	C ₁₂ H ₁₁ N ₃ O ₂ Se	24.22	25.62
23b	CH ₃ CO	<i>p</i> -CH ₃ C ₆ H ₄	136	C ₁₃ H ₁₃ N ₃ O ₂ Se	24.42	24.50
24a	C ₆ H ₅ CO	<i>p</i> -CH ₃ C ₆ H ₄	147	C ₁₄ H ₁₃ N ₃ O ₂ Se	20.50	20.54
24b	<i>p</i> -CH ₃ C ₆ H ₄ CO	C ₆ H ₅	135	C ₁₈ H ₁₅ N ₃ O ₂ Se	20.33	20.54
25a	C ₆ H ₅ OCO	C ₆ H ₅	90	C ₁₃ H ₁₃ N ₃ O ₃ Se	23.11	23.34
25b	C ₂ H ₅ OCO	<i>p</i> -CH ₃ C ₆ H ₄	210	C ₁₄ H ₁₃ N ₃ O ₃ Se	22.51	22.41
25c	C ₂ H ₅ OCO	<i>p</i> -ClC ₆ H ₄	141	C ₁₃ H ₁₂ ClN ₃ O ₃ Se	20.98	21.19
26a	C ₆ H ₅ NHCO	<i>p</i> -ClC ₆ H ₄	190	C ₁₇ H ₁₃ ClN ₄ O ₂ Se	18.77	18.81
26b	C ₆ H ₅ NHCO	<i>p</i> -CH ₃ C ₆ H ₄	175	C ₁₈ H ₁₆ N ₄ O ₂ Se	19.43	19.77
5- <i>N</i> -Benzoylimino-2,4-disubstituted- Δ^2 -1,3,4-selenadiazolines 27-31						
27	C ₆ H ₅	<i>p</i> -NO ₂ C ₆ H ₄	214	C ₂₁ H ₁₄ N ₄ O ₃ Se	17.52	17.57
28a	CH ₃ CO	C ₆ H ₅	239	C ₁₇ H ₁₃ N ₃ O ₂ Se	21.21	21.32
28b	CH ₃ CO	<i>p</i> -CH ₃ C ₆ H ₄	220	C ₁₈ H ₁₃ N ₃ O ₂ Se	20.40	20.54
29a	C ₆ H ₅ CO	<i>p</i> -CH ₃ C ₆ H ₄	227	C ₂₃ H ₁₇ N ₃ O ₂ Se	17.44	17.57
29b	<i>p</i> -CH ₃ C ₆ H ₄ CO	C ₆ H ₅	225	C ₂₂ H ₁₇ N ₃ O ₂ Se	17.50	17.57
30a	C ₂ H ₅ OCO	C ₆ H ₅	180	C ₁₈ H ₁₇ N ₃ O ₃ Se	19.65	19.72
30b	C ₂ H ₅ OCO	<i>p</i> -CH ₃ C ₆ H ₄	157	C ₁₈ H ₁₉ N ₃ O ₃ Se	19.10	19.06
30c	C ₂ H ₅ OCO	<i>p</i> -ClC ₆ H ₄	161	C ₁₈ H ₁₄ ClN ₃ O ₃ Se	18.62	18.16
31a	C ₆ H ₅ NHCO	<i>p</i> -ClC ₆ H ₄	250	C ₂₂ H ₁₃ ClN ₄ O ₂ Se	16.20	16.39
31b	C ₆ H ₅ NHCO	<i>p</i> -CH ₃ C ₆ H ₄	237	C ₂₃ H ₁₈ N ₄ O ₂ Se	17.02	17.11

Table 3

Electronic Absorption Maxima of Some Δ^2 -1,3,4-Selenadiazoline Derivatives in Ethanol

Compound No.	λ max nm (log ϵ)
9	350 (4.22), 253 (4.56)
11a	361 (4.13), 263 (4.31)
11b	362 (4.00), 265 (4.22)
12c	330 (4.00), 258 (4.02)
15b	480 (1.72), 281 (4.83), 253 (4.00)
16a	480 (1.78), 284 (3.86), 256 (3.99)
16b	480 (1.76), 283 (3.89), 255 (3.95)
17	480 (1.75), 342 (4.00), 268 (3.93)
19b	322 (4.02)
20a	325 (4.08)
20b	324 (4.07)
21	319 (3.98)
22	348 (4.22), 250 (4.40)
23a	320 (4.10), 258 (4.12)
23b	321 (4.07), 258 (4.14)
24a	322 (4.05), 257 (4.21)
24b	325 (4.01), 260 (4.23)
25a	318 (3.98)
27	347 (4.59), 256 (4.48)
28a	338 (4.25), 277 (4.16)
29a	345 (4.21), 279 (4.23)
29b	338 (4.11), 277 (4.21)
30c	333 (4.32), 252 (4.34)

The benzoylation of **9-13** was effected by refluxing equimolecular amounts of the imino compound and benzoyl chloride in pyridine (6

ml./mmole) for 25 minutes, cooled and poured on ice. Crystallization from acetic acid gave the corresponding benzoyl derivatives in 70% yield (Table 2).

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