

A. Shafiee (2), M. Vosooghi and I. Lalezari

Department of Chemistry, College of Pharmacy, Tehran University, Tehran, Iran

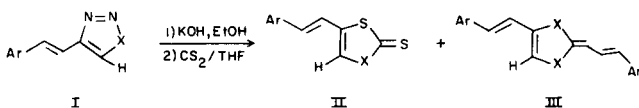
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4-Substituted vinyl and 4-(4-phenyl-1,3-butadienyl)-1,2,3-thiadiazoles were prepared through the reaction of 4-aryl-3-buten-2-one semicarbazone and 6-phenyl-3,5-hexadien-2-one semicarbazone with thionyl chloride, respectively. Decomposition of these 1,2,3-thiadiazoles as well as the corresponding 1,2,3-selenadiazoles with base and subsequent addition of carbon disulfide afforded 4-substituted vinyl 2-thioxo-1,3-dithioles and 5-substituted vinyl 2-thioxo-1,3-thiaselenoles.

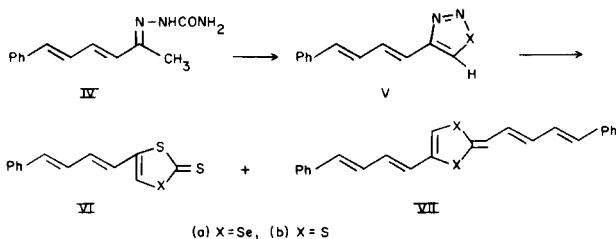
J. Heterocyclic Chem., 17, 545 (1980).

In continuation of the study on the chemistry of selenium heterocyclic compounds (3-8), we have recently reported a simple general method for the synthesis of 5-substituted 2-thioxo-1,3-thiaselenoles (9). In the present work, synthesis of 5-substituted vinyl 2-thioxo-1,3-thiaselenoles (II and IV, X = Se) and 4-substituted vinyl 2-thioxo-1,3-dithioles (II and VI, X = S) are reported.

The general method for the synthesis of 5-substituted 2-thioxo-1,3-thiaselenoles (9) was used for the preparation of compounds II and VI. The readily available 4-substituted vinyl and 4-(4-phenyl-1,3-butadienyl)-1,2,3-selenadiazoles (I and V, X = Se) were reacted with ethanolic potassium hydroxide and then carbon disulfide in tetrahydrofuran to give the desired compounds II (X = Se) and VI (X = S), respectively, in high yield. Small amounts of 1,4-diselenafulvenes were also isolated in these reactions (see Scheme I).



- (a) X = Se, Ar = Ph; (b) X = Se, Ar = p-BrC₆H₄-; (c) X = Se, Ar = p-ClC₆H₄-;
 (d) X = Se, Ar = p-CH₃C₆H₄-; (e) X = Se, Ar = p-CH₃OC₆H₄-; (f) X = Se,
 Ar = 3,4-Methylenedioxyphenyl; (g) X = Se, Ar = 2-Thienyl-; (h) X = S, Ar = Ph;
 (i) X = S, Ar = p-BrC₆H₄-; (j) X = S, Ar = p-ClC₆H₄-; (k) X = S, Ar = p-CH₃C₆H₄-;
 (l) X = S, Ar = p-CH₃OC₆H₄-; (m) X = S, Ar = 2-Thienyl



The nmr spectra of the 2-thioxo-1,3-thiaselenoles which were synthesized showed a sharp singlet at about δ 7.60 assigned to proton 4. This value was in agreement with our previous report (9).

The mass spectral fragmentation pattern for compounds II and VI (X = Se) was also in good agreement with the suggested structures. In the mass spectrum in addition to the strong molecular ion peak, strong peaks at M - 124 [M - (Se-C=S)], M - 156 [M - (CS₂Se)] and a weak peak at M - 76 [M - (CS₂)] were observed.

Reaction of the readily available 4-aryl- (or heterocyclic)-3-buten-2-one semicarbazones as well as that of 6-phenyl-3,5-hexadien-2-one semicarbazone (10) with thionyl chloride, according to our previously reported procedure (11), afforded the desired 1,2,3-thiadiazoles (I and V, X = S). The nmr spectra of the 1,2,3-thiadiazoles which were prepared showed a sharp singlet at about δ 8.40 assigned to proton 5.

Decomposition of 1,2,3-thiadiazoles (I and V, X = S) with ethanolic potassium hydroxide and subsequent addition of carbon disulfide in tetrahydrofuran afforded 4-substituted vinyl 2-thioxo-1,3-dithioles (II and VI, X = S) in good yield. Small amounts of 1,4-dithiofulvenes were also isolated.

The nmr spectra of the 2-thioxo-1,3-dithioles which were synthesized showed a sharp singlet at about δ 6.95 assigned to proton 5. This absorption is in accordance with the suggested structures.

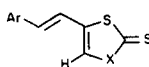
The mass spectral fragmentation pattern was also in good agreement with the suggested structure. In the mass spectrum, in addition to the strong molecular ion peak, strong peaks at M - 76 [M - CS₂] and M - 108 [M - CS₃] were observed.

The physical constants for the compounds which were prepared are summarized in Tables I and II.

EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and are uncorrected. Nmr spectra were determined using a Varian T-60 spectrometer and chemical shifts (δ) are in ppm relative to internal tetramethylsilane. Mass spectra were run on a Varian MAT-311 spectrometer at 70 eV.

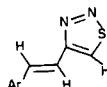
Table I



Compound No.	X	Ar	M.p.°C (a)	Yield %	Formula	C%		H%	
						Calcd.	Found	Calcd.	Found
IIa	Se	C ₆ H ₅ -	116-117	70	C ₁₁ H ₈ S ₂ Se	46.64	46.87	2.83	3.03
IIb	Se	<i>p</i> -BrC ₆ H ₄ -	173-175	65	C ₁₁ H ₇ BrS ₂ Se	36.46	36.23	1.93	1.68
IIc	Se	<i>p</i> -ClC ₆ H ₄ -	143-145	70	C ₁₁ H ₇ ClS ₂ Se	41.57	41.82	2.20	2.42
IId	Se	<i>p</i> -CH ₃ C ₆ H ₄ -	158-159	60	C ₁₂ H ₁₀ S ₂ Se	48.48	48.24	3.37	3.59
IIe	Se	<i>p</i> -CH ₃ OC ₆ H ₄ -	135-138 (b)	75	C ₁₂ H ₁₀ OS ₂ Se	46.01	45.78	3.19	3.42
IIf	Se	3,4-Methylenedioxyphenyl	205-207 (c)	65	C ₁₂ H ₈ O ₂ S ₂ Se	44.04	43.81	2.45	2.16
IIg	Se	2-Thienyl	118-120 (b)	80	C ₉ H ₆ S ₃ Se	37.37	37.63	2.08	2.26
IIh	S	C ₆ H ₅ -	115-117	75	C ₁₁ H ₈ S ₃	58.06	58.28	3.23	3.01
IIi	S	<i>p</i> -BrC ₆ H ₄ -	193-195	70	C ₁₁ H ₇ BrS ₃	41.90	42.15	2.22	2.41
IIj	S	<i>p</i> -ClC ₆ H ₄ -	187-188	70	C ₁₁ H ₇ ClS ₃	48.80	48.65	2.59	2.38
IIk	S	<i>p</i> -CH ₃ C ₆ H ₄ -	163-164	65	C ₁₂ H ₁₀ S ₃	57.60	57.86	4.00	3.78
III	S	<i>p</i> -CH ₃ OC ₆ H ₄ -	147-148	75	C ₁₂ H ₁₀ OS ₃	54.14	54.01	3.76	3.54
IIIm	S	2-Thienyl	138-139	80	C ₉ H ₆ S ₄	44.63	44.48	2.48	2.69
VIa	Se		143-145	75	C ₁₃ H ₁₀ S ₂ Se	50.49	50.71	3.24	3.45
VIb	S		144-145	75	C ₁₃ H ₁₀ S ₃	59.54	59.63	3.82	3.61

(a) Unless otherwise mentioned the compound was crystallized from carbon tetrachloride. (b) This compound was crystallized from ether. (c) This compound was crystallized from chloroform.

Table II



Compound (a) No.	Ar	M.p.°C (b)	Yield %	Formula	C%		H%		N%	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Ih	C ₆ H ₅ -	80-81	25	C ₁₀ H ₈ N ₂ S	63.83	63.65	4.26	4.02	14.89	14.68
Ii	<i>p</i> -BrC ₆ H ₄ -	182-185	20	C ₁₀ H ₇ BrN ₂ S	44.94	45.16	2.62	2.81	10.49	10.27
Ij	<i>p</i> -ClC ₆ H ₄ -	160-161 (c)	20	C ₁₀ H ₇ ClN ₂ S	53.93	54.15	3.15	3.01	12.58	12.34
Ik	<i>p</i> -CH ₃ C ₆ H ₄ -	105-107	28	C ₁₁ H ₁₀ N ₂ S	65.35	65.57	4.95	5.16	13.86	13.98
Il	<i>p</i> -CH ₃ OC ₆ H ₄ -	111-112	25	C ₁₁ H ₁₀ N ₂ OS	60.55	60.77	4.59	4.76	12.84	12.59
Im	2-Thienyl-	78-79	25	C ₈ H ₆ N ₂ S	49.48	49.69	3.09	3.28	14.43	14.65
Vb		124-126	18	C ₁₂ H ₁₀ N ₂ S	67.29	67.06	4.67	4.73	13.08	13.26

(a) Compounds Ia-Ig were reported previously (10). (b) Unless otherwise mentioned the compound was crystallized from ether. (c) This compound was crystallized from carbon tetrachloride.

5-Styryl 2-thioxo-1,3-thiaselenole (IIa).

To a stirred solution of 4-styryl-1,2,3-selenadiazole (10) (Ia, 235 mg., 1 mmole) in dioxane (5 ml.), a solution of potassium hydroxide (~0.3 g.) in ethanol (~2 ml.) was added, whereupon the evolution of nitrogen ceased. Tetrahydrofuran (5 ml.) and carbon disulfide (1 ml.) were added and stirring was continued for 1 hour at room temperature. The solvent was evaporated under reduced pressure. Water (10 ml.) was then added to the

residue and the mixture was extracted with chloroform (3 × 10 ml.). The extract was dried and the solvent distilled. The residue was purified by tlc (silica gel, chloroform:petroleum ether; 1:1). The fast moving fraction was crystallized from acetone to give 21 mg. (10%) of 2,ω-distyryl-1,4-diselenafulvene (IIIa), m.p. 179-184°, mixed melting point with an authentic sample, 179-184° (10). The slow moving fraction was crystallized from carbon tetrachloride to give 200 mg. (70%) of IIa (X = Se), m.p.

116-117° (carbon tetrachloride); nmr deuterochloroform: 7.63 (s, 1H, H₄), 7.45 (s, 5H, C₆H₅) and 6.78 ppm (AB q, 2H, ethylenic hydrogens, J = 16 Hz, the coupling constant confirms the *trans* configuration for the double bond); ms: m/e (relative intensity) 284 (M⁺, 96), 208 (6), 160 (53), 128 (100), 115 (37), 102 (18) and 78 (39).

Anal. Calcd. for C₁₁H₉S₂Se: C, 46.64; H, 2.83. Found: C, 46.87; H, 3.03.

Compounds IIb-IIg and VIa were prepared in a similar manner (see Table I).

4-Styryl-1,2,3-thiadiazole (Ih).

Thionyl chloride (4 ml.) was added to methyl styryl ketone semicarbazone (2.03 g., 0.01 mole). The mixture was heated gently until the evolution of gas started. After 30 minutes chloroform (50 ml.) was added, and the mixture was decomposed with an ice-cold saturated sodium bicarbonate solution. The mixture was filtered. The organic layer was washed with water, dried and evaporated. The residue was purified by tlc (silica gel, chloroform) and the product was crystallized from ether to give 0.47 g. (25%) of Ih, m.p. 80-81°; nmr (deuterochloroform): 8.36 (s, 1H, H₅), 7.50-6.67 ppm (m, 7H, aromatic and ethylenic).

Anal. Calcd. for C₁₀H₈N₂S: C, 63.83; H, 4.26; N, 14.89. Found: C, 63.65; H, 4.02; N, 14.68.

Other 4-substituted vinyl 1,2,3-thiadiazoles were prepared similarly (Table II).

4-Styryl-2-thioxo-1,3-dithiole (IIh).

To a stirred solution of 4-styryl-1,2,3-thiadiazole (Ih, 188 mg., 1 mmole) in dioxane (5 ml.), a solution of potassium hydroxide (~0.3 g.) in ethanol (~2 ml.) was added, whereupon the evolution of nitrogen ceased. Tetrahydrofuran (5 ml.) and carbon disulfide (1 ml.) were added and stirring was continued for 1 hour at room temperature. The solvent was evaporated under reduced pressure, water (10 ml.) was added to the residue, and the mixture was extracted with chloroform (3 × 10 ml.). The extract was dried and the solvent distilled. The residue was purified by tlc (silica gel, chloroform:petroleum ether, 1:1).

The fast moving fraction was crystallized from acetone to give 24 mg.

(15%) of 2,ω-distyryl-1,4-dithiafulvene, m.p. 214-215°.

Anal. Calcd. for C₂₀H₁₆S₂: C, 75.00; H, 5.00. Found: C, 75.21; H, 4.86.

The slow moving fraction was crystallized from carbon tetrachloride to give 177 mg. (75%) of IIh, m.p. 115-117°; nmr (deuterochloroform): 7.47 (s, 5H, aromatic), 6.96 (s, 1H, H₅), 6.80 ppm (AB q, 2H, ethylenic, J = 16 Hz, the coupling constant confirms the *trans* configuration for the double bond); ms: m/e (relative intensity) 236 (M⁺, 139), 204 (6), 160 (96), 128 (73) and 115 (97).

Compounds IIh-IIm and VIb were prepared in a similar manner (Table I).

Acknowledgment.

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