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SYNTHESIS AND REACTIONS OF SOME 2-THIENYL- AND 2-THENOYL-DERIVATIVES OF THIAZOLE AND THIADIAZOLINE AND THEIR SELENIUM ANALOGS

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SYNTHESIS AND REACTIONS OF SOME 2-THIENYL- AND 2-THENOYL-DERIVATIVES OF THIAZOLE AND THIADIAZOLINE AND THEIR SELENIUM ANALOGS

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2-(Thiocyanatoacetyl)thiophene **2** and its selenium analog **3** couple with diazotized anilines and yield 3-aryl-2-imino-5-(2-thenoyl)-2,3-dihydro-1,3,4-thiadiazoles **6** and 3-aryl-2-imino-5-(2-thenoyl)-2,3-dihydro-1,3,4-selenadiazoles **7** respectively. The reactions of both **6** and **7** with nitrous acid, acetic anhydride and benzoyl chloride are described. Azo coupling of 2-amino-4-(2-thienyl)thiazole **17** and its selenazole analog **18** with diazotized anilines yielded the arylazo derivatives **19** and **20** respectively. Reaction of the hydrazidoyl bromide **16** with potassium thiocyanate, potassium selenocyanate, thiourea and selenourea yields **6**, **7**, **19**, and **20** respectively.

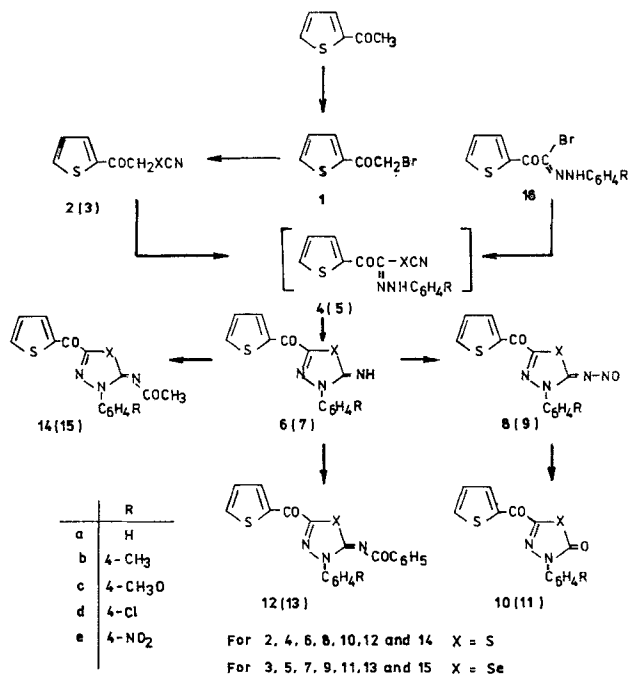
INTRODUCTION

Although 2-(thiocyanatoacetyl)thiophene **2** has been known for more than a century,¹ its chemistry has received so far little attention.²⁻⁵ Its selenium analog namely, 2-(selenocyanatoacetyl)thiophene **3** has not yet been reported. In this paper we wish to report a facile synthesis of **2** and **3** and the results of the study of their reactions with diazotized anilines.

DISCUSSION

The intermediate which seemed to be necessary for the preparation of **2** and **3** was 2-(bromoacetyl)thiophene **1** which has been prepared previously by bromination of 2-acetylthiophene in carbon disulfide¹ or in carbon tetrachloride in the presence of iron fillings.⁶ In this work, it was found more convenient to prepare compound **1** in almost quantitative yield by treatment of 2-acetylthiophene in ether with bromine in the presence of anhydrous aluminium chloride as catalyst (Scheme 1).

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SCHEME 1

Treatment of **1** with potassium thiocyanate in aqueous ethanol at room temperature afforded **2** in high yield. Compound **1** reacted with potassium selenocyanate under similar conditions to give 90% of the desired **3** (Scheme 1). Infrared spectrum of the new compound **3** showed a strong absorption bands near 2160 and 1660 cm^{-1} assignable to the selenocyanato and carbonyl groups respectively. The physical constants of **2** were identical in all respects with those reported in literature.²

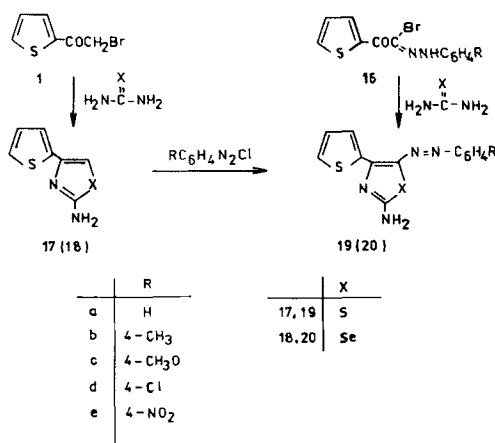
Treatment of **2** with diazotized anilines in pyridine gave 2-imino-2,3-dihydro-3-aryl-5-(2-thenoyl)-1,3,4-thiadiazoles **6a-e** in 80–90% yield. Under similar conditions **3** gives 2-imino-2,3-dihydro-3-aryl-5-(2-thenoyl)-1,3,4-selenazoles **7a-e** in high yield (Scheme 1). The structures of the products **6** and **7** were elucidated on the basis of their spectra, elemental analyses, alternate syntheses and by their reactions outlined in Scheme 1. For example, the infrared spectra of **6** and **7** revealed no bands in the 2000–2200 cm^{-1} region due to free SCN and SeCN groups, thus excluding the isomeric acyclic hydrazone structures **4** and **5**. The spectra showed, however, bands at 3345 (imino NH), 1640 (CO) and 1610 (C=N) cm^{-1} . The structures of **6** and **7** were further confirmed by their alternate synthesis. Thus treatment of the hydrazidoyl bromide **16** with potassium thiocyanate in ethanol at room temperature afforded **6**. Similar reaction of **16** with potassium selenocyanate yielded **7**. This finding suggests that both routes namely reaction of **2** (or **3**) with diazotized anilines and reaction of **16** with potassium thiocyanate (or potassium selenocyanate) involve the formation of **4**

(or **5**) as common intermediates respectively which cyclize into **6** (or **7**) as soon as they are formed.

Nitrosation of **6** and **7** gave the corresponding N-nitroso derivatives **8** and **9** respectively (Scheme 1). The structures of the latter products were substantiated by their elemental analyses and spectra. For example, their infrared spectra revealed the absence of the imino NH absorption but contained a common carbonyl absorption band near 1640 cm^{-1} . Upon refluxing in ethylene glycol compounds **8** and **9** decomposed and yielded the corresponding thiadiazolinones **10** and selenadiazolinones **11** respectively in almost quantitative yield. The infrared spectra of **10** and **11** showed in each case two common carbonyl bands near 1710 and 1640 cm^{-1} .

Acetylation of **6** and **7** with acetic anhydride yielded the corresponding N-acetyl derivatives **14** and **15** respectively. Both elemental and spectral data are consistent with their assigned structures. The ^1H nmr spectra of **14** and **15** revealed a common singlet signal near $\delta 2.37$ (3H, CH_3CO) ppm. Their infrared spectra showed bands at 1640 and 1625 cm^{-1} assignable to the 2-thenoyl and N-acetylimino carbonyl groups respectively. Treatment of **6** and **7** with benzoyl chloride in pyridine afforded the corresponding N-benzoyl derivatives **12** and **13** respectively. The structures of the latter products followed from their spectra and elemental analyses.

Reaction of **16** with excess thiourea in ethanol afforded products that were identified as 5-arylazo-4-(2-thienyl)-2-aminothiazoles **19** (Scheme 2). Similar treatment of **16** with excess selenourea under the same reaction conditions yielded 5-arylazo-4-(2-thienyl)-2-amino-selanazoles **20** (Scheme 2). The structures of both **19** and **20** were inferred from their elemental analyses, spectra and independent syntheses. For example, their infrared spectra showed no carbonyl absorption but exhibit characteristic bands near 3320 and 3470 cm^{-1} . The presence of the NH_2 group was confirmed by the appearance of an amino singlet at $\delta 5.98$ ppm in their ^1H nmr spectra. This signal disappeared upon shaking the solution of **19** or **20** in deuterated chloroform with deuterium oxide, and a new signal appeared at $\delta 4.50$ ppm assignable to DOH resonance. The structures of **19** and



SCHEME 2

20 were also substantiated by their independent synthesis by coupling of 2-amino-4-(2-thienyl)-substituted thiazole and selenazole **17** and **18** respectively with diazotized anilines (Scheme 2). The desired compounds **17** and **18** were prepared by the treatment of 2-(bromoacetyl)thiophene with thiourea and selenourea respectively (Scheme 2).

EXPERIMENTAL

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. The infrared spectra were recorded on a Unicam SP 1000 infrared spectrophotometer. The ^1H nmr spectra were measured in dimethyl sulfoxide- d_6 with a Varian EM-390 90 MHz spectrometer using tetramethylsilane as internal reference. Elemental analyses were performed at Microanalytical laboratory of Cairo University, Giza, Egypt. 2-Acetylthiophene was Aldrich reagent, and the hydrazidoyl bromides **16a–e** were prepared as previously described.⁷

Preparation of 2-bromoacetylthiophene (1). To a cold solution of 2-acetylthiophene (12.6 g, 0.1 mol) in dry ether (60 ml) was added anhydrous aluminum chloride (0.5 g) with stirring. To the resulting solution bromine (16 g, 0.1 mol) was added dropwise over a period of 15 min. After the addition was complete, the reaction mixture was poured into cold water (50 ml). The organic layer was separated, washed twice with water, then with dilute sodium bicarbonate solution (3 g in 50 ml of water) and finally dried over anhydrous sodium sulfate, then filtered. The solvent was evaporated under reduced pressure to afford 19.7 g (96%) of practically pure 2-bromoacetylthiophene. The physical constants of the oil obtained were identical with those reported in literature: b.p. 95–98°C/1.5 mm; n_D^{20} 1.6258⁶.

Preparation of 2-(thiocyanatoacetyl)thiophene (2) and 2-(selenocyanatoacetyl)thiophene (3). General Method. To a solution of **1** (10.26 g, 0.05 mol) in ethanol (50 ml) was added potassium thiocyanate (5.0 g, 0.05 mol) (or potassium selenocyanate (7.3 g, 0.05 mol)) in water (10 ml). The mixture was stirred at room temperature for 1 hour. The precipitated solid was collected, washed with water, dried and finally crystallized from ethanol.

Compound **2** had mp. 91°C (Lit. mp. 90–91°)⁶.

Compound **3** had mp. 105°C; IR(KBr): ν 2165 (SeCN), 1660 (CO) cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_5\text{NOSSe}$ (230.14): C, 36.53; H, 2.19; N, 6.09. Found: C, 36.31; H, 2.25; N, 6.18.

Preparation of 2-amino-4-(2-thienyl)thiazole (17) and 2-amino-4-(2-thienyl)selenazole (18). General Method. To a cold solution of 2-bromoacetylthiophene (5.13 g, 0.025 mol) in ethanol (20 ml) was added thiourea or selenourea (0.03 mol). The reaction mixture was stirred for 15 minutes, then refluxed for 2 hours on a water bath, and cooled. The mixture was made alkaline with sodium hydroxide solution while stirring. The free precipitated base was collected, washed with water and crystallized from dilute ethanol or pyridine.

Compound **17** was obtained in 94% yield, mp. 139–140°, IR(KBr): ν 3460, 3300 (NH_2), 1630 ($\text{C}=\text{N}$) cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_6\text{N}_2\text{S}_2$ (182.27): C, 46.12; H, 3.32; N, 15.37; S, 35.18. Found: C, 45.91; H, 3.30; N, 15.16; S, 34.88.

Compound **18** was obtained in 91% yield, mp. 145°C; IR(KBr) ν 3460, 3300 (NH_2), 1625 ($\text{C}=\text{N}$) cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_6\text{N}_2\text{SSe}$ (229.16): C, 36.69; H, 2.62; N, 12.23; S, 13.99. Found: C, 36.38; H, 2.51; N, 12.00; S, 14.15.

Preparation of 3-Aryl-2-imino-5-(2-thienyl)-2,3-dihydro-1,3,4-thiadiazoles 6a–e and selenadiazoles 7a–e. method A—To a cold solution **2** (or **3**) (0.01 mol) in pyridine (50 ml) was added the appropriate arenediazonium chloride solution (0.01 mol) while stirring. After the addition was complete, the mixture was left in refrigeration for 4 hours. The solid formed was collected and crystallized from ethanol or aqueous pyridine. The compounds prepared together with their physical constants are listed in Table I.

Method B—To a solution of the appropriate hydrazidoyl bromide **16** (0.005 mol) in ethanol (50 ml) was added a solution of potassium thiocyanate (0.01 mol) (or potassium selenocyanate (0.01 mol)) in water (10 ml) and the mixture was refluxed for 1 hour. The cold reaction mixture was diluted with water. The precipitated solid was collected, washed with water and crystallized from ethanol to give the corresponding **6** (or **7**). The compounds prepared by this method were identical in all respects (mp., mixture mp., and spectra) with those obtained above by method A (Table I).

TABLE I

3-Aryl-2-imino-2,3-dihydro-5-(2-thenoyl)-1,3,4-thiadiazoles **6** and 3-Aryl-2-imino-2,3-dihydro-5-(2-thenoyl)-1,3,4-selenadiazoles **7**

Comp. no.	M.P. °C	Yield %	Formula (M.W.)	Analysis calcd/found				
				C	H	N	S	Cl
6a	150	85	C ₁₃ H ₉ N ₃ OS ₂ (287.35)	54.33 53.90	3.16 3.23	14.62 14.35	22.31 22.18	
6b	155	88	C ₁₄ H ₁₁ N ₃ OS ₂ (301.38)	55.79 56.10	3.70 3.66	13.94 14.15		
6c	174	81	C ₁₄ H ₁₁ N ₃ O ₂ S ₂ (317.38)	52.98 53.15	3.49 3.50	13.24 13.11	20.21 20.46	
6d	212	90	C ₁₃ H ₈ ClN ₃ OS ₂ (321.80)	48.52 48.21	2.50 2.44	13.06 12.86		11.02 11.23
6e	253	86	C ₁₃ H ₈ N ₄ O ₃ S ₂ (332.35)	46.97 46.73	2.43 2.35	16.86 16.67		
7a	170	83	C ₁₃ H ₉ N ₃ OSSe (334.25)	46.71 46.48	2.71 2.53	12.57 12.31	9.59 9.27	
7b	175	85	C ₁₄ H ₁₁ N ₃ OSSe (348.27)	48.28 48.51	3.18 3.10	12.06 11.85	9.21 9.10	
7c	168	80	C ₁₄ H ₁₁ N ₃ O ₂ SSe (364.27)	46.16 45.87	3.04 3.25	11.53 11.29	8.80 8.62	
7d	216	87	C ₁₃ H ₈ ClN ₃ OSSe (368.69)	42.35 42.31	2.19 2.33	11.40 11.27	8.70 8.53	9.61 9.75
7e	226	84	C ₁₃ H ₈ N ₄ O ₃ SSe (379.25)	41.17 41.25	2.13 2.15	14.77 14.65	8.45 8.34	

TABLE II

3-Aryl-2-N-nitrosoimino-2,3-dihydro-5-(2-thenoyl)-1,3,4-thiadiazoles **8** and 2-N-nitrosoimino-2,3-dihydro-1,3,4-selenadiazoles **9**

Comp. no.	M.P. °C	Yield %	Formula (M.W.)	Analysis calcd/found				
				C	H	N	S	Cl
8a	148	95	C ₁₃ H ₈ N ₄ O ₂ S ₂ (316.35)	49.35 49.11	2.55 2.29	17.71 17.43	20.27 19.93	
8b	126	98	C ₁₄ H ₁₀ N ₄ O ₂ S ₂ (330.38)	50.89 51.15	3.05 3.27	16.96 16.85	19.41 19.69	
8c	144	93	C ₁₄ H ₁₀ N ₄ O ₃ S ₂ (346.38)	48.54 48.27	2.91 2.67	16.17 15.96	18.51 18.37	
8d	164	96	C ₁₃ H ₇ ClN ₄ O ₂ S ₂ (350.79)	44.51 44.29	2.01 2.25	15.97 15.82	18.28 18.11	10.11 10.21
8e	179	94	C ₁₃ H ₇ N ₅ O ₄ S ₂ (361.34)	43.21 43.35	1.95 2.10	19.38 19.11	17.74 17.49	
9a	138	91	C ₁₃ H ₈ N ₄ O ₂ SSe (363.25)	42.98 43.21	2.22 2.15	15.42 15.40	8.83 8.62	
9b	142	93	C ₁₄ H ₁₀ N ₄ O ₂ SSe (377.27)	44.57 44.52	2.67 2.53	14.85 14.63	8.50 8.35	
9d	132	92	C ₁₃ H ₇ ClN ₄ O ₂ SSe (397.69)	39.26 39.30	1.77 1.92	14.07 14.15	8.06 8.21	8.91 8.87
9e	158	94	C ₁₃ H ₇ N ₅ O ₄ SSe (408.25)	38.24 38.12	1.73 1.75	17.16 17.11	7.85 7.67	

Nitrosation of 6 and 7. To a solution of **6** (or **7**) (0.005 mol) in acetic acid (30 ml) was added a cold sodium nitrite solution (0.7 g in 10 ml water) dropwise while stirring. The mixture was left in ice bath for 4 hours. The reddish solid that precipitated was collected. Crystallization of the crude product from methanol gave the corresponding nitroso derivative **8** and **9** (Table II).

Thermolysis of 8 and 9. The appropriate nitroso derivative **8** (or **9**) (1 g) was refluxed in ethylene glycol (20 ml) till its red color disappeared (20 minutes) and cooled. Dilution with water precipitated the corresponding thiadiazolinone **10** (or selenadiazolinone **11**). The crude product was collected, washed with water and crystallized from dimethylformamide–water mixture (1:1 v/v). The products **10** and **11** prepared are listed together with their physical constants in Table III.

Acylation of 6a and 7a. A solution of **6a** (or **7a**) (0.005 mol) in acetic anhydride (25 ml) was refluxed for 1 hour. The solvent was removed under reduced pressure and the residue was triturated with water. The solid formed was collected, washed with water and crystallized from acetic acid to give the N-acetyl derivative **14a** (85%). Similar treatment of **7a** yielded **15a** (80%).

Compound **14a** had mp. 180°C, IR(KBr) ν 1640, 1625 (CO) cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2$ (329.38): C, 54.69; H, 3.37; N, 12.76; S, 19.47. Found: C, 54.33; H, 3.16; N, 12.57; S, 19.12.

Compound **15a** had mp. 165°C, IR(KBr) ν 1640, 1625 (CO). Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_2\text{SSe}$ (376.28): C, 47.88; H, 2.95; N, 11.17. Found: C, 47.56; H, 3.17; N, 11.25.

Treatment of **6a** (or **7a**) (0.005 mol) with benzoyl chloride (0.005 mol) in pyridine (30 ml) at reflux for 30 minutes and work up of the reaction mixture in the usual way gave the corresponding benzoyl derivatives **12a** and **13a** in 90–92% yield.

Compound **12a** had mp. 255°C (DMF), IR(KBr) ν 1640, 1625 (CO) cm^{-1} . Anal. Calcd. for $\text{C}_{20}\text{H}_{13}\text{N}_3\text{O}_2\text{S}_2$ (391.45): C, 61.36; H, 3.35; N, 10.74; S, 16.38. Found: C, 61.58; H, 3.41; N, 10.45; S, 16.18.

Compound **15a** had mp. 253°C (DMF), IR(KBr) ν 1640, 1625 (CO) cm^{-1} . Anal. Calcd. for $\text{C}_{20}\text{H}_{13}\text{N}_3\text{O}_2\text{SSe}$ (448.34): C, 53.57; H, 2.92; N, 9.37. Found: C, 53.34; H, 3.17; N, 9.15.

Preparation of 19 and 20. Method A—To a cold ethanolic solution of **17** (or **18**) (0.01 mol) buffered with sodium acetate (3 g) was added a solution of the appropriate diazotized aniline (0.01 mol) dropwise over a period of 45 minutes with stirring at 0–5°C. After the addition was complete the mixture was left for 4 hours in ice bath. The colored solid that precipitated was collected, washed with water, dried and crystalized from aqueous pyridine to give the arylazo derivatives **19** and **20** (Table IV).

TABLE III

3-Aryl-5-(2-thenoyl)-2,3-dihydro-1,3,4-thiadiazol-2-ones **10** and 3-Aryl-5-(2-thenoyl)-2,3-dihydro-1,3,4-selenadiazol-2-ones **11**

Comp. no.	M.P. °C	Yield %	Formula (M.W)	Analysis calcd/found				
				C	H	N	S	Cl
10a	159	96	$\text{C}_{13}\text{H}_8\text{N}_2\text{O}_2\text{S}_2$ (288.34)	54.15 53.95	2.80 2.76	9.72 9.64	22.24 22.00	
10b	157	98	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_2$ (302.37)	55.61 55.42	3.33 3.41	9.27 9.15	21.21 21.37	
10c	162	96	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_3\text{S}_2$ (318.37)	52.81 53.17	3.17 3.23	8.80 8.80		
10d	166	98	$\text{C}_{13}\text{H}_7\text{ClN}_2\text{O}_2\text{S}_2$ (322.79)	48.37 48.00	2.18 2.33	8.68 8.81		10.98 10.84
10e	210	97	$\text{C}_{13}\text{H}_7\text{N}_3\text{O}_4\text{S}_2$ (333.34)	46.84 47.10	2.12 2.10	12.60 12.45	19.24 19.38	
11a	171	91	$\text{C}_{13}\text{H}_8\text{N}_2\text{O}_2\text{SSe}$ (335.24)	46.57 46.82	2.40 2.37	8.36 8.17	9.56 9.68	
11b	168	94	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{SSe}$ (349.26)	48.41 48.30	2.89 3.00	8.02 7.88	9.18 9.35	
11d	177	95	$\text{C}_{13}\text{H}_7\text{ClN}_2\text{O}_2\text{SSe}$ (369.70)	42.23 42.51	1.91 2.12	7.58 7.77	8.67 8.53	9.59 9.50
11e	230	95	$\text{C}_{13}\text{H}_7\text{N}_3\text{O}_4\text{SSe}$ (380.23)	41.06 40.85	1.85 1.73	11.05 10.90	8.44 8.65	

TABLE IV
5-Arylazo-4-(2-thienyl)-2-aminothiazoles **19** and 5-Arylazo-4-(2-thienyl)-2-aminoselenazoles **20**

Comp. no.	M.P. C°	Yield %	Formula (M.W.)	Analysis calcd/found				
				C	H	N	S	Cl
19a	213	85	C ₁₃ H ₁₀ N ₄ S ₂ (286.37)	54.52 54.35	3.52 3.51	19.56 19.49	22.39 22.13	
19b	216	87	C ₁₄ H ₁₂ N ₄ S ₂ (300.40)	55.97 56.21	4.03 4.20	18.65 18.73	21.35 21.54	
19c	220	71	C ₁₄ H ₁₂ N ₄ OS ₂ (316.40)	53.14 52.87	3.82 3.61	17.71 18.00	20.27 19.95	
19d	254	86	C ₁₃ H ₉ ClN ₄ S ₂ (320.81)	48.66 48.75	2.83 2.87	17.46 17.29		11.05 11.20
20a	182	78	C ₁₃ H ₁₀ N ₄ SSe (333.26)	46.85 46.51	3.02 3.16	16.81 16.64	9.62 9.47	
20b	179	83	C ₁₄ H ₁₂ N ₄ SSe (347.29)	48.41 48.56	3.48 3.45	16.13 15.88	9.23 9.36	
20c	164	68	C ₁₄ H ₁₂ N ₄ OSSe (363.29)	46.28 45.93	3.33 3.21	15.42 15.24	8.83 9.04	
20d	200	84	C ₁₃ H ₉ ClN ₄ SSe (367.71)	42.46 42.33	2.47 2.51	15.24 15.13		9.64 9.72
20e	241	82	C ₁₃ H ₉ N ₅ O ₂ SSe (378.27)	41.27 41.35	2.40 2.31	18.51 18.35	8.48 8.55	

Method B—To solution of the appropriate hydrazidoyl bromide **16** (0.005 mol) in ethanol (40 ml) was added thiourea (or selenourea) (0.01 mol). The mixture was refluxed for 20 hours and filtered while hot. The filtrate was poured onto crushed ice. The colored solid that precipitated was collected washed with water, and finally crystallized from ethanol or aqueous pyridine. The compounds obtained by this method were identical in all respects (mp., mixture mp., ir spectra) with those prepared by method A above.

REFERENCES

1. H. Brunswig, *Chem. Ber.* **19**, 2890 (1886).
2. W. S. Emerson and T. M. Patrick, *J. Org. Chem.*, **13**, 722 (1948).
3. H. P. Derible and L. Taliani, *Fr. Demande*, **2**, 146, 161; *Chem. Abstr.* **79**, 78789q (1973).
4. G. Seybold and B. Wuerzer, *Ger. Offen.*, *DE* **3**, 142, 727; *Chem. Abstr.* **99**, 53778k (1983).
5. A. G. Bayer, Belg. 818, 293; *Chem. abstr.*, **84**, 58923d (1976).
6. F. Kipnis, H. Soloway and J. Ornfelt, *J. Am. Chem. Soc.*, **71**, 10 (1949).
7. A. M. Farag and M. S. Algharib, *Org. Prep. Proc. Int.*, **20**, (1988) in press.