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Reaction with Hydrazonoyl Halides XXIII [1]: Synthesis and Reactions of C-Coumarinoyl-*N*-arylformohydrazonoyl Bromides

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ABSTRACT: *C-Coumarinoyl-N-arylformohydrazonoyl bromides (**3**) were synthesized by reaction of N-nitrosoarylacetamides with an appropriate sulfonium bromide in ethanol at room temperature. The reactions of potassium thiocyanate, potassium selenocyanate, thiourea, methyl phenylthiocarbomate, and methyl phenylhydrazinedithioate with hydrazonoyl bromide* **3a** *were examined.*© 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 355–362, 1999

Previously, α-(3-coumarinyl)-*β*-bromoglyoxal-2-phenylhydrazone (**3a**) was claimed [2] to be obtained in 60% yield by the coupling of benzenediazonium chloride with the sulfonium bromide [2] **2** in acetic acid containing sodium acetate (Scheme 1). Surprisingly, when this procedure was repeated, the product isolated showed chemical and physical behavior completely nonconsistent with the previously proposed structure **3a**. The product was found to be identical in all respects (m.p., mixed m.p., IR, and 1H NMR) with 3-(*ω*-bromoacetyl)coumarin (**1**) [3].

In the present investigation, **3a** was successfully prepared by the reaction *N*-nitrosoacetanilide [4] with sulfonium bromide **2** in ethanol. The probable mechanism that accounts for the foregoing reaction is presented in Scheme 1. It is assumed that the configuration of the hydrazone intermediate **5** is stabilized in nonaqueous solvents by intramolecular hydrogen bonding, and nucleophilic attack by the bromide ion produces **3**. Also, the sulfonium salt **2** reacts with the appropriate *N*-nitrosoarylacetamides **4b–e** in ethanol at room temperature to afford the hydrazonoyl bromides **3b–e**, respectively. The reactions of **3** with each of potassium thiocyanate, potassium selenocyanate, thiourea, methyl phenylthiocarbamate, and methyl phenylhydrazinedithioate were used to shed more light on its correct structure.

Treatment of hydrazonoyl bromide **3a** with potassium thiocyanate or potassium selenocyanate in ethanol at room temperature gave one isolable product, in each case, identified as 2-imino-5-coumarin-3′-oyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazole (**9a**) and 2-imino-5-coumarin-3′-oyl-3-phenyl-2,3-dihydro-1,3,4-selenadiazole (**10a**), respectively. The structures were deduced from their spectra and their chemical behavior that is described below (cf. Scheme 2). The IR (cm^{-1}) spectra of the products revealed no band at 2000–2200 due to the -SCN (or SeCN) group [5]. The spectra contained bands near 3250 (NH), 1720, 1660 (two CO), and 1620 (C=N). The ^1H NMR (δ) spectrum of **9a** showed signals at 7.31–8.10 (m, 10H, ArH's) and 9.31 (s, br., 1H, NH). Upon shaking with D_2O, the singlet at 9.31 disappeared and a new signal appeared at 4.38 assignable to DOH proton resonance. The structure **9** (or **10**) was further confirmed by independent synthesis. Thus, treatment of 3-(*ω*-thiocyanatoacetyl)coumarin (**19**) or 3-(*ω*-selenocyanatoacetyl)coumarin (**20**) with benzenediazonium chloride in ethanolic sodium acetate solution produced a product, in each case, identical in all respects (m.p., mixed m.p., and

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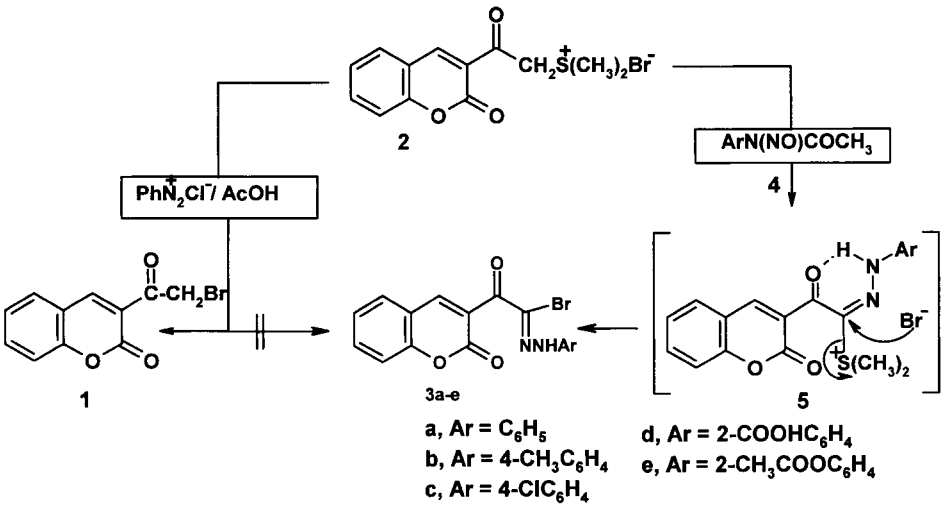
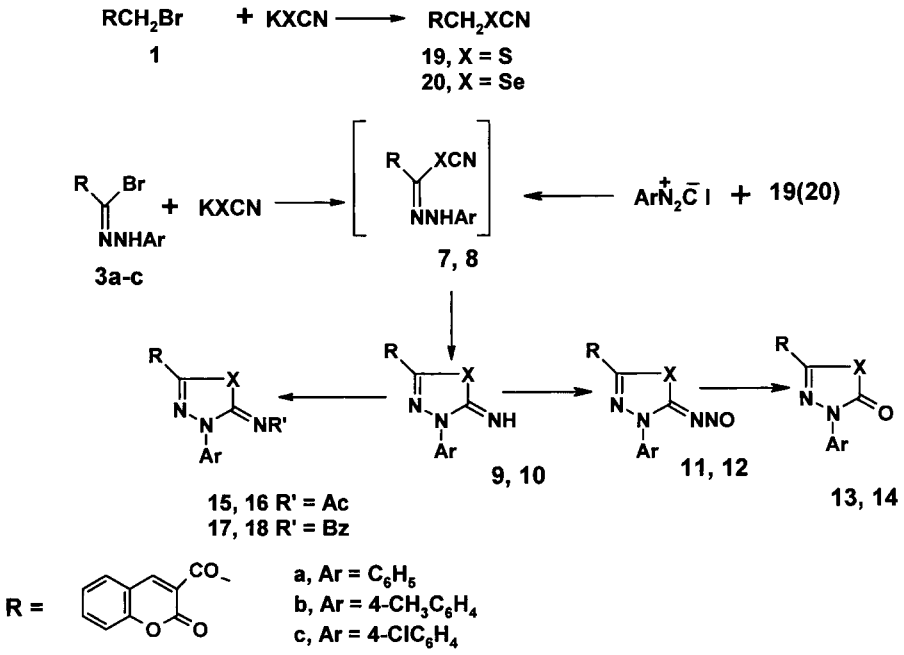


SCHEME 1



SCHEME 2

spectra) with the corresponding **9a** and **10a**, respectively. Such results indicate that both the azo coupling of **19** (or **20**) and the reaction of **3a** with potassium thiocyanate (or potassium selenocyanate) proceed through the common intermediate **7** (or **8**), which cyclizes readily under the reaction conditions to give **9** or **10**. Similarly, the reaction of **3b,c** with potassium thiocyanate in ethanol afforded **9b** and **9c**, respectively (cf. Scheme 2).

Nitrosation of each **9** and **10** gave the nitroso derivatives **11** and **12**, respectively. The IR (cm^{-1}) spectra of each **11** and **12** showed no NH band but contained in common two carbonyl bands at 1720 and 1660 and a band near 1550 (NO). The ^1H NMR (δ) spectrum of **11b** showed signals at 2.43 (s, 3H, 4-$CH_3C_6H_4$) and 7.20–7.59 (m, 9H, ArH's). All nitroso compounds decomposed to the corresponding 2,3-dihydrothiadiazoles **13** and 2,3-dihydroslenadiazoles **14**, respectively, upon refluxing in xylene. The structures of the products **13** and **14** were confirmed on the basis of elemental analysis and spectral studies. Thus, the IR (cm^{-1}) spectra of each **13** and **14** revealed bands near 1740, 1700, and 1643 (3 CO's). The ^1H NMR (δ) spectrum of **13b** shows signals at

2.43 (s, 3H, 4-$CH_3C_6H_4$) and 7.15–7.78 (m, 9H, ArH's).

Acylation of **9** and **10** with acetic anhydride (and benzoyl chloride in pyridine) afforded the corresponding N-acetyl- (and N-benzoyl-) **15,17** and **16,18**, respectively. The structures **15–18** were established on the basis of elemental analyses and spectral data. Thus, the IR (cm^{-1}) spectra of products **15–18** revealed bands near 1740, 1650, 1635 (3 CO's), and 1608 (C=N). The ^1H NMR (δ) spectra of **15a** showed signals at 2.35 (s, 3H, $CH_3CON=$), 7.26–7.85 (m, 9H, ArH's), and 8.33 (s, 1H, coumarin H-4).

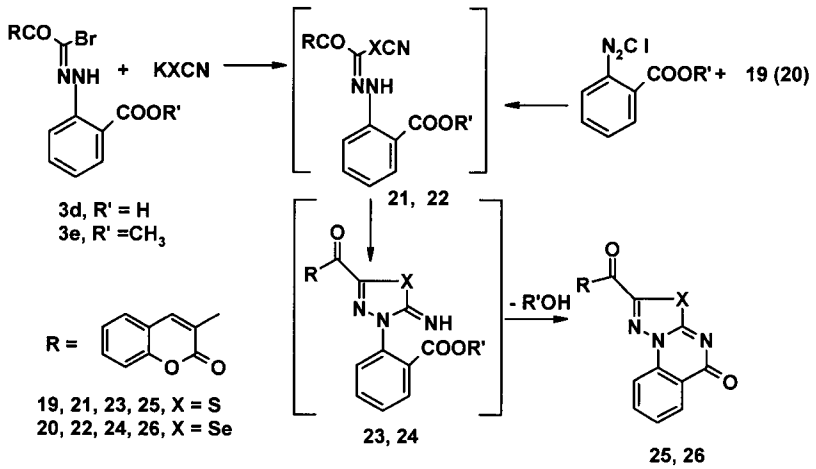
Also, hydrazonoyl bromides **3d** and **3e** reacted with each of potassium thiocyanate and potassium selenocyanate in ethanol at room temperature to afford one product in each case, identical in all respects (m.p., mixed m.p., IR, ^1H NMR) with each other and having molecular formulas $C_{19}H_9N_3O_4S$ and $C_{19}H_9N_3O_4Se$, respectively. The IR (cm^{-1}) spectra of the products revealed bands near 1740, 1670, 1640 (3 CO's) and no absorption bands between 3500 and 3300 or 2300 and 2200 due to the absence of NH and -SCN (or -SeCN) groups.

The ^1H NMR δ value of each product showed one signal due to ArH's protons. From the previous data, the products are formulated as 3-coumarin-3′-oyl-2,3-dihydro-1,3,4-thiadiazolo[3,2-*a*]quinazolin7-one (**25**) and 3-coumarin-3′-oyl-2,3-dihydro-1,3,4-selenadiazolo[3,2-*a*]quinazolin-7-one (**26**), respectively. Compounds **25** and **26** were also obtained via coupling of each of 3-(ω-thiocyanatoacetyl)coumarin (**19**) and 3-(ω-selenocyanatoacetyl)coumarin (**20**) with diazotized anthranilic acid or its methyl ester in ethanolic sodium acetate solution (cf. Scheme 3). The compatible mechanism is thought to involve the spontaneous cyclization of **21** (or **22**) to yield the iminothiadiazoline **23** (or iminoselenadiazoline **24**), which complete the reaction by the loss of the elements of water or methanol to afford the final product **25** (or **26**).

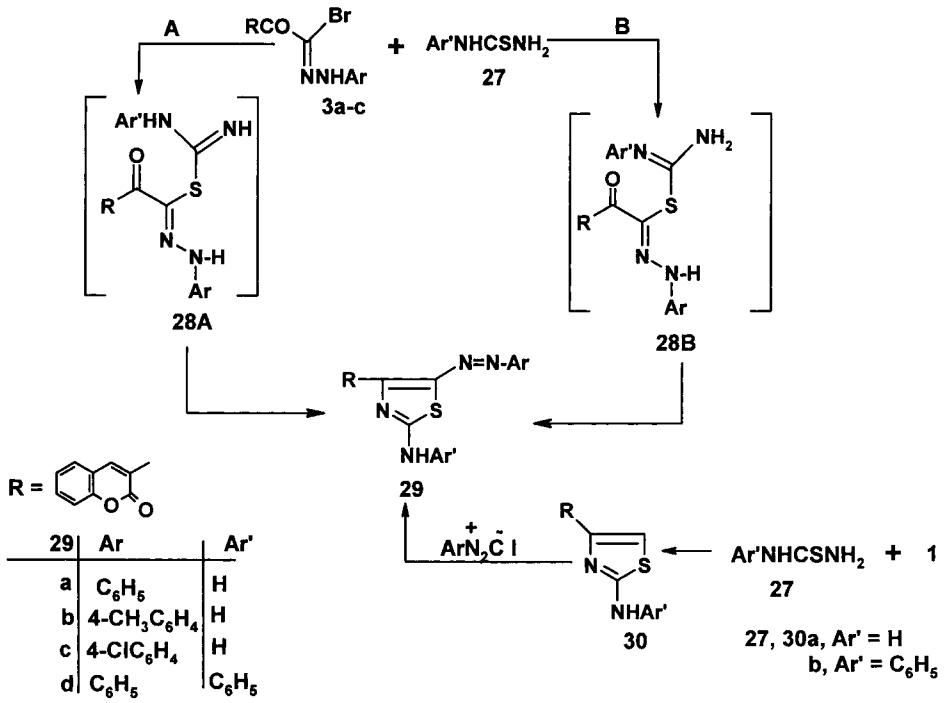
Next, treatment of thiourea or phenylthiourea with the appropriate hydrazonoyl bromides **3a–c** in ethanolic triethylamine gave one isolable product in each case.

The IR (cm^{-1}) spectra of these products revealed bands near 3430, 3280 (NH_2), and 1740 (coumarin CO). The ^1H NMR (δ) spectrum of the product (**3a** used) showed signals at 5.93 (s, br., 2H, NH_2), 7.25–7.81 (m, 9H, ArH's), and 8.30 (s, 1H, coumarin H-4). When the compound was shaken with D_2O, the signals at 5.93 disappeared, and a new signal at 4.65 appeared due to DOH. Thus, the structure was formulated as 2-amino-4-coumarinyl-5-phenylazothiazole (**29a**). This assignment was supported by our finding that **29a** was also obtained from coupling of 2-amino-4-coumarinylthiazole [3] (**30a**) with benzenediazonium chloride in pyridine solution (cf. Scheme 4). It is assumed that the first step involves formation of a carbon sulfur link by elimination of a molecule of hydrogen bromide to give **28A** or **28B**, by analogy with the reaction of thioamides with α-halogenated compounds [6]. In the second step, ring closure occurs through a direct attack by either the imino or amino nitrogen atom on the carbonyl carbon with one molecule of water being eliminated.

On the other hand, the hydrazonoyl bromide **3a** reacted with each of methyl phenylthiocarbamate [7] **31a** [or methyl phenylhydrazinedithioate [8] (**31b**)] in ethanolic triethylamine to give one isolable product according to TLC. The product was formulated as 5-coumarin-3′-oyl-2-iminophenyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazole (**35a**) and 5-coumarin-3′-oyl-3-phenyl-2-phenylhydrazono-2,3-dihydro-1,3.4-thiadiazole (**35b**), respectively. The ^1H



SCHEME 3



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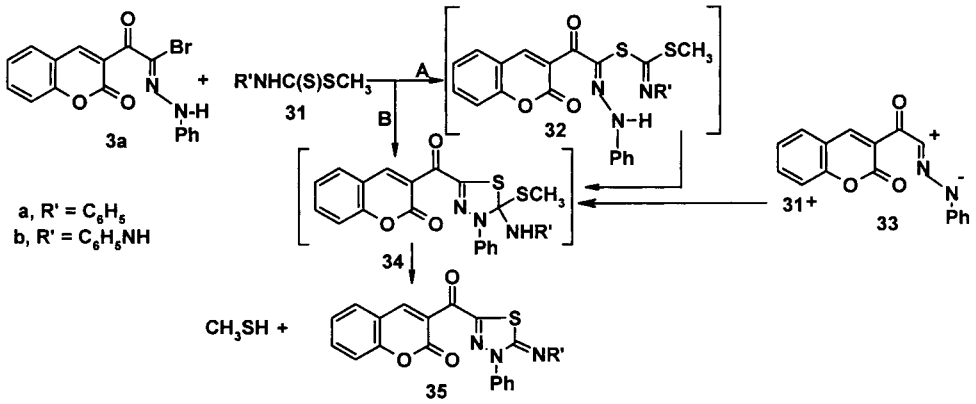

SCHEME 5

NMR (δ) spectrum of **35a** showed signals at 7.23–8.13 (m, 14H, ArH's) and 8.34 (s, 1H, coumarin H-4), and its IR (cm^{-1}) spectrum revealed no band between 3500 and 3100 attributable to the absence of an NH group and 1732, 1649 (two CO's). The ^1H NMR (δ) spectrum of **35b** showed signals at 7.72–8.12 (m, 15H, ArH's, and NH) and 8.35 (s, 1H, coumarin H-4). Its IR (cm^{-1}) spectrum revealed bands at 3271 (NH); 1728, 1654 (2 CO's). Based on the elemental analysis and spectral data, the reaction can be explained to involve elimination of methane thiol from the cycloadduct **34**, which formed by addition of the nitrile imide **33** (prepared in situ by reaction of **3a** with triethylamine) to the CS double bond or by formation of a cyclic hydrazone **32** by elimination of one molecule of hydrogen bromide from **3a** and **31a** (or **31b**) (cf. Scheme 5).

EXPERMINTAL

All melting points were determined on an electrothermal apparatus and are uncorrected. IR (cm^{-1}) spectra were recorded on KBr discs on an FT IR-8201 PC Shimadzu spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ on a Gemini 200 MHz spectrometer using TMS as an internal refer-

TABLE 1 Characterization Data of the Newly Synthesized Compounds

Compd	*M.p. (°C) Color*	*Mol. Formula Mol. Wt.*	*% Analyses, Calcd./Found* *C*	*H*	*N*	*S*
3a	228–230	$C_{17}H_{11}BrN_2O_3$[a]	55.01	2.99	7.55	
	yellow	371.19	55.20	2.90	7.40	
3b	225–227	$C_{18}H_{13}BrN_2O_3$[a]	56.12	3.40	7.27	
	yellow	385.22	56.10	3.50	7.20	
3c	238–240	$C_{17}H_{10}BrClN_2O_3$[a]	50.34	2.48	6.91	
	yellow	405.64	50.40	2.40	6.80	
3d	256–258	$C_{18}H_{11}BrN_2O_5$[e]	52.07	2.67	6.75	
	yellow	415.20	52.20	2.60	6.60	
3e	235–237	$C_{19}H_{13}BrN_2O_5$[a]	53.17	3.05	6.53	
	yellow	429.23	53.10	3.20	6.60	
9a	188–190	$C_{18}H_{11}N_3O_3S$[e]	61.88	3.17	12.02	9.17
	yellow	349.37	61.80	3.00	12.20	9.30
9b	128–130	$C_{19}H_{13}N_3O_3S$[e]	62.80	3.61	11.56	8.82
	yellow	363.40	62.70	3.50	11.60	8.70
9c	138–140	$C_{18}H_{10}ClN_3O_3S$[e]	56.33	2.62	10.95	8.35
	yellow	383.82	56.20	2.70	11.10	8.50
10a	175–177	$C_{18}H_{11}N_3O_3Se$[e]	54.55	2.80	10.60	
	yellow	396.27	54.50	2.60	10.40	
11a	145 (d)	$C_{18}H_{10}N_4O_4S$[a]	57.14	2.66	14.81	8.47
	red	378.37	57.30	2.60	14.79	8.40
11b	125 (d)	$C_{19}H_{12}O_4S$[e]	58.16	3.08	14.27	8.17
	red	392.40	58.10	3.20	14.10	8.40
11c	133 (d)	$C_{18}H_9ClN_4O_4S$[e]	52.37	2.20	13.57	7.77
	red	412.81	52.20	2.30	13.50	7.60
12a	152 (d)	$C_{18}H_{10}N_4O_4Se$[e]	50.84	2.37	13.17	
	red	425.26	50.70	2.20	13.30	
13a	186–188	$C_{18}H_{10}N_2O_4S$[a]	61.70	2.88	8.00	9.15
	golden yellow	350.35	61.60	2.70	7.90	9.00
13b	172–174	$C_{19}H_{12}ClN_2O_4S$[a]	62.62	3.31	7.69	8.80
	pale yellow	364.38	62.50	3.40	7.50	8.70
13c	178–180	$C_{18}H_9N_2ClO_4S$[a]	56.19	2.36	7.28	8.33
	pale yellow	384.80	56.30	2.20	7.20	8.20
14a	185–187	$C_{18}H_{10}N_2O_4Se$[a]	54.42	2.54	7.05	
	pale yellow	397.25	54.40	2.40	7.10	
15a	183–185	$C_{20}H_{13}N_3O_4S$[a]	61.37	3.35	10.74	8.19
	redish yellow	391.41	61.30	3.50	10.60	8.20
15b	171–173	$C_{21}H_{15}N_3O_4S$[a]	62.21	3.73	10.36	7.90
	yellow	405.44	62.10	3.60	10.20	7.80
15c	188–190	$C_{20}H_{12}ClN_3O_4S$[a]	56.41	2.84	9.87	7.53
	pale yellow	425.86	56.30	2.70	9.80	7.60
16a	195–197	$C_{20}H_{13}N_3O_4Se$[a]	54.81	2.99	9.59	
	pale yellow	438.30	54.80	3.00	9.50	
17a	263–265	$C_{25}H_{15}N_3O_4S$[c]	66.22	3.33	9.27	7.07
	orange	453.48	66.20	3.50	9.20	7.20
17b	223–225	$C_{26}H_{17}N_3O_4S$[a]	66.80	3.67	8.99	6.86
	greenish yellow	467.51	66.70	3.80	8.90	6.90
17c	251–253	$C_{25}H_{14}ClN_3O_4S$[c]	61.53	2.89	8.61	6.57
	yellow	487.93	61.40	2.90	8.60	6.50
18a	265–267	$C_{25}H_{15}N_3O_4Se$[a]	60.01	3.02	8.40	
	yellow	500.38	66.10	3.10	8.20	
19	173–175[123]	$C_{12}H_7NO_3S$[e]	58.77	2.88	5.71	13.07
	pale yellow	245.26	58.70	2.90	5.70	13.10
20	123–125	$C_{12}H_7NO_3Se$[a]	49.33	2.42	4.79	
	pale yellow	292.15	49.20	2.50	4.70	
25	308–310	$C_{19}H_9N_3O_4S$[c]	60.80	2.42	11.19	8.54
	golden yellow	375.37	60.80	2.30	11.10	8.60
26	300–302	$C_{19}H_9N_3O_4Se$[e]	54.04	2.15	9.95	
	pale yellow	422.26	54.20	2.20	9.90	
29a	291–293	$C_{18}H_{12}N_4O_2S$[d]	62.06	3.47	16.08	9.20
	red	348.39	62.20	3.40	16.10	9.20

TABLE 1 (Continued) Characterization Data of the Newly Synthesized Compounds

Compd	M.p. (°C) Color	% Analyses, Calcd./Found Mol. Formula Mol. Wt.	C	H	N	S
29b	296–298	$C_{19}H_{14}N_4O_2S^d$	62.97	3.89	15.46	8.85
	red	362.41	62.90	3.90	15.40	8.70
29c	298–300	$C_{18}H_{11}ClN_4O_2S^d$	56.47	2.90	14.63	8.36
	brown	382.83	56.50	2.90	14.50	8.30
29d	273–275	$C_{24}H_{16}N_4O_2S^d$	67.91	3.80	13.20	7.55
	red	424.48	67.80	3.80	13.10	7.40
30b	206–208	$C_{18}H_{12}N_2O_2S^e$	67.48	3.78	8.74	10.01
	greenish yellow	320.37	67.50	3.70	8.70	10.20
35a	185–186	$C_{24}H_{15}N_3O_3S^e$	67.75	3.55	9.88	7.54
	yellow	425.47	67.70	3.60	9.80	7.40
35b	202–204	$C_{24}H_{16}N_4O_3S^a$	65.44	3.66	12.72	7.28
	dark brown	440.48	65.30	3.60	12.90	7.10

a = acetic acid; c = N,N-dimethylformamide; d = dioxan; e = ethanol.

ence, and chemical shifts are expressed as δ units. Elemental analyses were performed at the microanalytical center, Cairo University.

Synthesis of α-(3-Coumarinyl)-β-bromoglyoxal-2-arylhydrazone (**3a–e**)

A mixture of the sulfonium bromide **2** [2] (32.9 g, 0.1 mol) and the appropriate *N*-nitrosoacetarylamides (0.15 mol) in ethanol (150 mL) was stirred for 2 hours at room temperature. The reaction mixture was left overnight, then diluted with water (50 mL). The precipitated solid was collected and crystallized from acetic acid (cf. Tables 1 and 2).

Synthesis of 2,3-Dihydro-1,3,4-thiadiazoles (**9a–c**)*, 2,3-Dihydroselenadiazole* (**10a**)*, 2,3-Dihydrothiadiazolo[3,2-a]quinazolinone* (**25**)*, and 2,3-Dihydroselenadiazolo[3,2-a]quinazolinone* (**26**)

Method (*A*). A solution of potassium thiocyanate or potassium selenocyanate (0.005 mol) in water (5 mL) was added to a solution of the appropriate hydrazonoyl bromide **3a–e** (0.005 mol) in ethanol (30 mL) with stirring. The reaction mixture was stirred for 4 hours at room temperature. During this period, the material went into solution, and a new solid precipitated. The latter was collected, washed with water, and crystallized from a proper solvent (cf. Tables 1 and 2).

Method (*B*). A cold solution of the appropriate compounds 3-(ω-thiocyanatoacetyl)coumarin **19** or 3-(ω-selenocyanatoacetyl)coumarin **20** (0.01 mol) and sodium acetate trihydrate (1.3 g, 0.01 mol) in ethanol (50 mL) was treated, with stirring, with the appropriate diazotized primary aromatic amines (0.01 mol) and left in the ice chest for 8 hours. The solid formed was collected, washed with water, and then crystallized from ethanol. All compounds prepared by this method were identical in all respects (m.p., mixed m.p., and spectra) with those prepared in *Method A*.

Nitrosation of Each **9a–c** *and* **10**

The appropriate of **9a–c** or **10** (1 g) in acetic acid (30 mL) was treated with a saturated solution of sodium nitrite with stirring (30 min). The reddish product that precipitated was collected and crystallized from ethanol. Compounds **11a–c** and **12** were obtained in 65–77% yield (cf. Tables 1 and 2).

Synthesis of **13a–c** *and* **14**

The appropriate nitroso derivatives **11a–c** and **12** (1.0 g) were refluxed in xylene (30 mL) for 30 minutes then left overnight at room temperature. The solvent was removed, and a small amount of ethanol was added to the residue. The precipitate that formed was collected and then crystallized from a proper solvent. The products **13a–c** and **14** obtained in 70–72% yields, with their physical properties, are listed in Tables 1 and and 2.

Acylation of **9a–c** *and* **10**

The appropriate compounds **9a–c** and **10** (1.0 g) were stirred in acetic anhydride (10 mL) for 30 minutes [or boiled with benzoyl chloride in pyridine (10 mL)] and poured onto crushed ice (50 g). The crude

TABLE 2 IR and ^{1}H NMR Data of the Newly Synthesized Compounds

Compd.	*IR* (cm^{-1})	^{1}*H NMR* (δ)
3a	3240 (NH), 1724, 1658 (CO's)	7.12–7.97(m, 10H, ArH's and coumarin H-4) and 8.56(s, br., 1H, NH).
3b	3238 (NH), 1732, 1655 (CO's), and 1610 (NH).	2.45(s, 3H, 4-$CH_3C_6H_4$), 7.12–7.97(m, 9H, ArH's and coumarin H-4), and 8.56(s, br., 1H, NH).
3c	3236 (NH), 1726, 1662 (CO's), and 1610 (C = N).	7.12–7.97(m, 10H, ArH's and coumarin H-4) and 8.56(s, br., 1H, NH).
3d	3230 (NH), 3146–2530(OH), 1735, 1714, 1668 (CO's), and 1606(C = N).	7.12–7.97(m, 9H, ArH's and coumarin H-4), 8.56(s, br., 1H, NH), and 12.18(s, 1H, COOH).
3e	3184(NH), 1728, 1697, 1664 (CO's), and 1606(C = N).	3.97(s, 3H, OCH_3) and 7.03–8.06(m, 10H, ArH's, coumarin H-4, and NH proton).
9b	3221(NH), 1743, 1645(CO's), and 1610(C = N).	2.45(s, 3H, 4-$CH_3C_6H_4$), 7.31–8.10(m, 9H, ArH's, and coumarin H-4), and 9.31(s, br., 1H, NH).
9c	3256(NH), 1732, 1655(CO's), and 1606(C = N).	7.31–8.10(m, 9H, ArH's and coumarin H-4) and 9.31(s, br., 1H, NH).
10a	3317(NH), 1720, 1645(CO's), and 1606(C = N).	7.31–8.10(m, 10H, ArH's and coumarin H-4) and 9.31(s, br., 1H, NH).
11a	1735, 1658(CO's), 1608(C = N), and 1525(NO).	7.20–7.59(m, ArH's, and coumarin H-4).
11c	1747, 1651(CO's), 1606(C = N), and 1650(NO).	7.20–7.59(m, arH's, and coumarin H-4).
12a	1745, 1645(CO's), 1606(C = N), and 1560(NO).	7.22–7.64(m, ArH's, and coumarin H-4).
13a	1647, 1705, 1643(CO's), and 1608(C = N).	7.22–7.76(m, ArH's, and coumarin H-4).
13c	1749, 1708, 1654(CO's), and 1608(C = N).	7.22–7.72(m, ArH's, and coumarin H-4).
14a	1743, 1705, 1639(CO's), and 1608(C = N).	7.21–7.82(m, ArH's, and coumarin H-4).
15b	1747, 1651, 1631(CO's), and 1608(C = N).	2.45(s, 3H, 4-$CH_3C_6H_4$), 2.35(s, 3H, CH_3 CON =), 7.26–7.85(m, 8H, ArH's), and 8.33(s, 1H, coumarin H-4).
15c	1716, 1662, 1636(CO's), and 1608(C = N).	2.34(s, 3H, CH_3CON =), 7.22–7.80(m, 9H, ArH's), and 8.35(s, 1H, coumarin H-4).
16a	1734, 1676, 1651(CO), and 1604(C = N).	2.36(s, 3H, CH_3CON =), 7.22–7.84(m, 9H, ArH's), and 8.37(s, 1H, coumarin H-4).
17a	1735, 1658(CO's), and 1608(NH).	7.22–7.84(m, 14H, ArH's) and 8.37(s, 1H, coumarin H-4).
17b	1747, 1649, 1631(CO's), and 1614(C = N).	2.45(s, 3H, 4-$CH_3C_6H_4$), 7.26–7.85(m, 13H, ArH's), and 8.33(s, 1H, coumarin H-4).
17c	1735, 1656, 1627(CO's), and 1608(C = N).	7.22–7.84(m, 13H, ArH's) and 8.37(s, 1H, coumarin H-4).
18a	1726, 1676, 1651(CO's), and 1608(C = N).	7.22–7.84(m, 8H, ArH's) and 8.37(s, 1H, coumarin H-4).
19	2156(SCN), 1730, 1675 (CO's), and 1608(C = N).)	4.66(s, 2H, CH_2), 7.22–7.55(m, 4H, ArH's), and 8.37(s, 1H, coumarin H-4).
20	2152(SCN), 1732, 1685(CO's), and 1608(C = N).	4.63(s, 2H, CH_2), 7.22–7.55(m, 4H, ArH's), and 8.33(s, 1H, coumarin H-4).
25	1747, 1662, 1651(CO's), and 1604(C = N).	7.22–7.72(m, 8H, ArH's) and 8.30(s, 1H, coumarin H-4).
29b	3433, 3278(NH_2), 1737(CO), and 1606(C = N).	2.45(s, 3H, 4-CH3C6H4), 5.93(s, br., 2H, NH_2), 7.25–7.81(m, 8H, ArH's), and 8.30(s, 1H, coumarin H-4).
29c	3438, 3288(NH_2), 1737(CO), and 1606(C = N).	5.93(s, br., 2H, NH_2), 7.25–7.81(m, 8H, ArH's), and 8.30(s, 1H, coumarin H-4).
29d	3166(NH), 1733(CO), and 1608(C = N).	7.25–7.81(m, 14H, ArH's), 8.30(s, 1H, coumarin H-4), and 9.22(s, 1H, NH).

solid that precipitated was collected and crystallized from acetic acid or dimethylformamide in 67–68% yields. Compounds 15–18 that had been prepared, together with their physical constants, are listed in Tables 1 and 2.

Synthesis of 3-(ω-Thiocyanatoacetyl)coumarin (**19**) *or 3-(ω-Selenocyanato)acetylcoumarin* (**20**)

A mixture of equimolar quantities of 3-(ω-bromoacetyl)coumarin (**1**) and potassium thiocyanate or potassium selenocyanate (0.05 mol each), in ethanol (50 mL) was stirred for 4 hours at room temperature. The solid, so formed, was collected and then crystallized from ethanol to give **19** and **20** in 70–72% yield, respectively (cf. Tables 1 and 2).

Synthesis of 2-Aminothiazole **30a,b**

Equimolar amounts of 3-(ω-bromoacetyl)coumarin and thiourea (or phenylthiourea) (0.05 mol each), in ethanol (80 mL) were refluxed for 2 hours. The solid

formed was collected and washed with ethanol. The solid was boiled in water containing sodium acetate for 2 hours, then collected by filtration, washed with water, and crystallized from ethanol to give **30a,b**, respectively, in 78% yieled (cf. Tables 1 and 2).

Synthesis of 5-Arylazothiazoles **29**

Method (*A*). To a solution of thioura or phenylthiourea (0.005 mol) in ethanol (30 mL), a solution of the appropriate hydrazonoyl bromide **3a–c** (0.005 mol) and triethylamine (0.7 mL, 0.005 mol) was added with stirring. The reaction mixture was refluxed for 4 hours, cooled, then poured into cold water (50 mL containing two drops of ammonium hydroxide). The solid that precipitated was collected, washed with water, and crystallized from dioxane, in 58–60% yields (cf. Tables 1 and 2).

Method (*B*). A cold solution of the appropriate **30a,b** (0.01 mol) in pyridine (30 mL) was treated, with stirring, with the appropriate diazotized primary aromatic amines (0.01 mol) and left in the ice chest for 3 hours. The solid that formed was collected, washed with water, and then crystallized from dioxane to give **29** in 72–74% yields. All compounds prepared by this method are identical in all respects (m.p., mixed m.p., and spectra) with those prepared by Method (A).

Synthesis of 2,3-Dihydro-1,3,4-thiadiazoles (**35a,b**)*: General Procedure*

To a solution of the appropriate dithiocarbazate **31a,b** and the hydrazonoyl bromide **3a** (5 mmol each) in ethanol (20 mL) was added triethylamine (0.7 mL, 5 mmol), at room temperature with stirring. Stirring was continued for 2 hours, and the resulting solid was collected, washed with water, and crystallized from acetic acid to give **35a,b,** respectively in 70–75% yields (cf. Tables 1 and 2).

REFERENCES

[1] Part XXII Abdelhamid, A. O.; Abed, N. M.; Al-Fayez, F. M., Phosphorus Sulfur Relat Elem 1999, in press.
[2] Ismail, N. A.; Khalifa, F. A.; Magd Eldin, A. A., Heterocycles 1991, 32, 1101–1107.
[3] Koelsch, C. F. J Am Chem Soc 1950, 72, 2993–95.
[4] Fischer, O. Chem Ber 1876, 9, 463; Wechsler, H. Liebigs Ann 1902, 325, 237–8.
[5] Bellamy, L. J. The Infrared Spectra of Complex Molecules, Methuen & Co.: New York, 1969.
[6] Wiley, R. H.; England, D. C.; Beher, L. C. Organic Reactions; Wiley: New York, 1951; Vol. 6, pp 367–407.
[7] Ottenbrite, R. M. J Chem Soc Perpkin Trans 1 1972, 88–90.
[8] Bazavova, I. M.; Dubenko, R. G.; Pelkis, P. S. Zh Org Khim 1982, 18, 213–17.