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 Nnitrosoarylacetamides 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-2phenylhydrazone (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 hydrazonovl 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 D₂O, 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 $3-(\omega-\text{selenocyanatoacetyl})$ 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-CH₃C₆H₄) and 7.20–7.59 (m, 9H, ArH's). All nitroso compounds decomposed to the corresponding 2,3dihydrothiadiazoles 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-CH₃C₆H₄) 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, CH₃CON=), 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 (NH₂), and 1740 (coumarin CO). The ¹H NMR (δ) spectrum of the product (3a used) showed signals at 5.93 (s, br., 2H, NH₂), 7.25-7.81 (m, 9H, ArH's), and 8.30 (s, 1H, coumarin H-4). When the compound was shaken with D₂O, 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



SCHEME 4



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 CDCl₃ on a Gemini 200 MHz spectrometer using TMS as an internal refer-

			% Analyses, Calcd.	/Found			-
3a 228-230 yellow Cr,H,BN,Q ⁺ 371 19 55.01 55.0 2.99 7.40 75.5 3b 225-227 Cr,H,BN,Q ⁺ yellow 56.12 3.40 7.27 3c 238-240 Cr,H,BN,Q ⁺ yellow 50.34 2.48 6.91 3d 226-258 Cr,H,BN,Q ⁺ yellow 52.07 2.67 6.75 3d 226-258 Cr,H,BN,Q ⁺ yellow 53.10 3.20 6.60 3e 236-237 Cr,H,BN,Q ⁺ yellow 53.10 3.20 6.60 3e 188-190 Cr,H,N,Q,S ⁺ yellow 53.31 3.20 6.60 3e 183-22 52.07 2.67 3.50 11.60 8.7 3b 222 56.13 3.01 12.02 9.1 9.3 3b 225 52.07 2.61 11.60 8.7 9.3 3c yellow 33.32 56.33 2.62 10.60 9.3 3c yellow 33.32 57.14 2.66 11.8 8.4 </th <th>Compd</th> <th>M.p. (°C) Color</th> <th>Mol. Formula Mol. Wt.</th> <th>С</th> <th>Н</th> <th>N</th> <th>S</th>	Compd	M.p. (°C) Color	Mol. Formula Mol. Wt.	С	Н	N	S
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	3a	228–230	$C_{17}H_{11}BrN_2O_3^{a}$	55.01	2.99	7.55	
3b 226-227 C _u H _u Br(V,Q ₁ [*]) 56.12 3.40 7.27 3c 238-22 56.10 3.50 7.20 3c 238-240 C _u H _u Br(DN,Q ₁ [*]) 50.34 2.48 6.91 3d 266-258 C _u H _u Br(N,Q ₁ [*]) 52.07 2.67 6.75 3e 238-237 C _u H _u Br(N,Q ₂ [*]) 53.10 3.22 6.60 9a 188-190 C _u H _u Br(N,Q ₂ [*]) 63.17 3.06 6.53 9b 128-70 C _u H _u Br(N,Q ₂ [*]) 61.88 3.17 1.60 8.75 9c 138-140 C _u H _u CN,Q ₅ * 61.88 3.17 1.60 8.75 9c 138-140 C _u H _u CN,Q ₅ * 56.12 2.00 1.16 8.75 9c 138-140 C _u H _u CN,Q ₅ * 57.42 2.66 14.84 8.42 9c 138-140 C _u H _u CN,Q ₅ * 57.30 2.00 10.60 55.57 10a 3.52 7.77 red 3.37		yellow	371.19	55.20	2.90	7.40	
	3b	225–227 vollow	$C_{18}H_{13}BrN_2O_3^{a}$	56.12	3.40	7.27	
Corr Corr <th< th=""><td>30</td><td>238-240</td><td>C H BrCIN O ª</td><td>50.10 50.34</td><td>3.50</td><td>7.20</td><td></td></th<>	30	238-240	C H BrCIN O ª	50.10 50.34	3.50	7.20	
	50	vellow	405.64	50.40	2.40	6.80	
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	3d	256–258	$C_{18}H_{11}BrN_2O_5^{e}$	52.07	2.67	6.75	
3e 23-237 C _w H ₀ H ₀ N ₀ A ⁺ 429-23 55.17 3.05 6.63 9a 188-190 C _w H ₀ N ₀ S ⁺ 61.88 3.17 12.02 9.17 9b 128-130 C _w H ₀ N ₀ S ⁺ 61.88 3.17 12.02 9.33 9b 128-130 C _w H ₀ N ₀ S ⁺ 62.80 3.61 11.60 8.73 9c 138-140 C _w H ₀ CN ₀ S ⁺ 65.33 2.62 10.95 8.33 9ellow 383.82 65.20 2.70 11.10 8.55 10a 175-177 C _w H ₀ N ₀ S ⁺ 54.55 2.80 10.60 11b 125 (d) C _w H ₀ O,S ⁺ 53.16 3.08 14.27 8.11 12a 133 (d) C _w H ₀ O,S ⁺ 53.16 3.08 14.27 8.17 12a 152 (d) C _w H ₀ O,S ⁺ 53.16 3.08 14.27 8.17 12a 152 (d) C _w H ₀ O,S ⁺ 53.37 3.17 7.77 12a 152 (d) <th< th=""><td></td><td>yellow</td><td>415.20</td><td>52.20</td><td>2.60</td><td>6.60</td><td></td></th<>		yellow	415.20	52.20	2.60	6.60	
yellow 429.23 53.10 3.20 6.60 yellow 349.37 61.80 3.00 12.20 9.17 yellow 363.40 62.70 3.50 11.66 8.82 yellow 363.40 62.70 3.50 11.66 8.72 yellow 383.82 56.20 2.70 11.16 8.53 yellow 386.27 54.55 2.80 10.60 11a 145.(d) C. ₂ H ₁ ,N,O,S ^{as} 55.13 2.66 14.81 8.47 11b 125.(d) C. ₂ H ₁ ,Q,S ^{as} 58.16 3.08 14.27 8.17 11c 133.(d) C. ₂ H ₁ ,Q,S ^{as} 52.37 2.20 13.57 7.76 12a 152.(d) C. ₃ H ₁ ,Q,S ^{as} 61.70 2.88 8.00 9.16 12a 152.(d) C. ₃ H ₁ ,Q,Q,S ^{as} 61.70 2.88 8.00 9.16 13a 186-188 C. ₃ H ₁ ,Q,Q,S ^{as} 61.70 2.88 8.00 9.16	3e	235–237	$C_{19}H_{13}BrN_2O_5^a$	53.17	3.05	6.53	
a non-riso C ₁₀ +1, NO, S ^a 01.88 3.11 12.22 9.13 g 122-130 C ₁₀ +1, NO, S ^a 62.80 3.61 11.66 8.22 g valiow 363.40 62.70 3.50 11.60 8.77 g 138-140 C ₁₀ +1, NO, S ^a 65.33 2.62 10.85 11.60 8.77 g valiow 383.82 55.20 2.60 10.40 7.71 7.	00	yellow	429.23	53.10	3.20	6.60	0.17
9b 128-30 yellow C _a H ₁ N ₁ O ₂ S ² 62.80 62.70 3.61 3.61 11.66 8.70 8.70 8.70 9c 138-140 C _a H ₁ ClM ₂ O ₃ S ² 56.33 2.62 10.95 8.33 yellow 383.82 56.20 2.70 11.10 8.55 yellow 396.27 54.55 2.80 10.60 yellow 396.27 54.55 2.80 10.60 yellow 396.27 54.55 2.80 10.40 red 378.37 57.30 2.60 14.79 8.44 red 392.40 58.16 3.08 14.27 8.77 red 412.81 52.27 2.20 13.50 7.66 12a 152 (d) C ₄ H ₁ O, O, S ⁵ 61.70 2.88 8.00 9.16 golden yellow 350.35 61.60 2.70 7.90 9.00 13a 186–188 C ₄ H ₁ O, O, S ⁵ 62.62 3.31 7.68 8.00 golden yellow 384.80	Ja	vellow	349.37	61.80	3.00	12.02	9.17
yellow 263.30 62.70 3.50 11.60 8.72 9c 138-140 C ₂₄ H ₄ (N,O,S ^a) 56.20 2.70 11.10 8.50 10a 175-177 C ₄ H ₄ (N,O,S ^a) 54.55 2.80 10.60 11a 145 (d) C ₆ H ₄ (N,O,S ^a) 57.14 2.66 14.81 8.47 11b 125 (d) C ₆ H ₄ (N,O,S ^a) 57.14 2.66 14.81 8.47 11b 125 (d) C ₆ H ₄ (N,O,S ^a) 58.16 3.08 14.27 8.17 red 392.40 58.16 3.20 14.10 8.44 11c 133 (d) C ₆ H ₄ (N,O,S ^a) 50.37 2.20 13.57 7.77 red 425.26 50.84 2.37 13.17 70 9.00 9.05 9.33 766 7.0 7.90 9.00 9.16 9.16 7.2 8.80 9.15 9.16 9.16 7.20 8.20 9.16 9.236 7.20 8.20 8.33	9b	128–130	C10H12N2O2Se	62.80	3.61	11.56	8.82
9c 138–140 C _µ H _µ ClN _Q O ₅ ^{sc} 56.33 2.62 10.95 8.32 10a 175–177 C _µ H _µ N _Q O ₅ ^{sc} 56.455 2.80 10.60 11a 145 (d) C _µ H _µ N _Q O ₅ ^{sc} 57.14 2.66 14.81 8.40 11b 125 (d) C _µ H _µ N _Q O ₅ ^{sc} 57.14 2.66 14.81 8.40 11c 133 (d) C _µ H _µ N _Q O ₅ ^{sc} 57.30 2.20 13.50 7.67 red 392.40 58.10 3.20 14.10 8.40 11c 133 (d) C _µ H _µ O _µ O _µ O ₅ ^{sc} 50.84 2.37 13.17 red 425.26 50.70 2.20 13.30 9.00 13a 186–188 C _µ H _µ N _µ O _µ O ₅ ^{sc} 66.160 2.70 7.90 9.00 13b 172–174 C _µ H _µ O _µ O _µ O ₅ ^{sc} 66.160 2.70 7.90 9.00 13b 172–174 C _µ H _µ O _µ O _µ O ₅ ^{sc} 56.19 2.36 7.28 8.33 gold		yellow	³ 363.40 [°]	62.70	3.50	11.60	8.70
yellow383.8256.202.7011.108.5010a175-177C _H H,NO,Se54.552.8010.6011a145 (d)C _H H,NO,S*57.142.6614.818.4711b125 (d)C _H H,Q,S*58.163.0814.278.1711cred392.4058.103.2014.108.4411c133 (d)C ₀ H,CIN,Q,S*52.372.2013.577.77red412.8152.202.3013.507.6612a152 (d)C ₀ H,M,NO,S*61.702.288.009.16golden yellow350.3561.602.707.909.0013b172-174C ₁₀ H,Q,Q,S*62.623.317.698.62pale yellow363.3561.602.707.909.0013b172-174C ₁₀ H,Q,Q,S*66.192.367.288.37pale yellow364.3862.503.407.508.70pale yellow397.2554.402.407.101615a183-185C ₂₀ H,N,Q,S*66.133.5010.608.2015b171-173C ₂₀ H,Q,Q,S*66.133.5510.607.999.0016a185-187C ₂₀ H,Q,Q,S*66.133.5510.748.1615b171-173C ₂₀ H,Q,Q,S*66.302.707.208.2015c188-190C ₂₀ H,G,Q,S*66.213.339.077.6315a <td< th=""><td>9c</td><td>138–140</td><td>$C_{18}H_{10}CIN_3O_3S^e$</td><td>56.33</td><td>2.62</td><td>10.95</td><td>8.35</td></td<>	9c	138–140	$C_{18}H_{10}CIN_3O_3S^e$	56.33	2.62	10.95	8.35
10a 1/5-1/7 C _u H ₁ ,M ₂ O ₂ Se ^a 54:55 2.80 10.80 11a 145 (d) C _u H ₁ ,N ₂ O ₂ S ^a 57.14 2.66 14.81 8.47 11b 125 (d) C _u H ₁ ,O ₂ S ^a 57.30 2.60 14.79 8.44 11b 126 (d) C _u H ₁ ,O ₂ S ^a 58.16 3.08 14.27 8.17 11c 133 (d) C _u H ₁ ,O ₁ S ^a 52.37 2.20 13.57 7.77 red 412.81 52.20 2.30 13.50 7.66 red 425.26 50.70 2.20 13.30 9.00 13a 186-188 C _u H ₁ ,Q,Q,S ^a 62.62 3.31 7.69 8.60 golden yellow 364.38 62.50 3.40 7.50 8.73 13a 172-174 C _u H ₁ ,Q,Q,S ^a 66.19 2.36 7.28 8.33 golden yellow 364.38 62.50 3.40 7.60 8.70 13a 185-187 C _u H ₁ ,N,O ₂ S ^a	40	yellow	383.82	56.20	2.70	11.10	8.50
yellow 340,2/2 54-30 2.00 10-40 red 378,37 57,30 2.60 14.79 8.44 red 378,37 57,30 2.60 14.79 8.44 red 392,40 58.10 3.08 14.27 8.17 red 392,40 58.10 3.20 14.10 8.44 red 412,81 52.20 2.30 13.50 7.67 12a 152 (d) C. ₁ H. ₁₀ N,Q.Se ^a 50.84 2.37 13.17 golden yellow 350.35 61.60 2.70 7.90 9.00 3b 172–174 C. ₁₀ H. ₂ CIN,Q.S ^a 62.62 3.31 7.69 8.80 pale yellow 364.38 62.50 3.40 7.50 8.77 3c 172–174 C. ₁₀ H. ₂ N,Q.S ^a 66.19 2.36 7.28 8.33 pale yellow 397.25 54.40 2.40 7.10 8.20 13c 185–187 C. ₁₄ H. ₃ N,Q.S ^a	10a	1/5–1// vollow	C ₁₈ H ₁₁ N ₃ O ₃ Se ^e	54.55	2.80	10.60	
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	11a	145 (d)	C. H. N.O. Sª	57 14	2.00	14.81	8 47
11b 125 (d) C., H., O., S ^a 58.16 3.08 14.27 8.17 red 392.40 58.10 3.20 14.10 8.40 red 412.81 52.20 2.30 13.57 7.77 red 412.81 52.20 2.33 13.17 7.60 red 425.26 50.70 2.20 13.30 7.60 golden yellow 350.35 61.60 2.70 7.90 9.00 13b 172–174 C., H., CIN, O, S ^a 62.62 3.40 7.50 8.70 golden yellow 364.38 62.50 3.40 7.50 8.70 13c 178–180 C., H, N, O, S ^a 61.37 3.35 10.74 8.16 pale yellow 391.41 61.30 3.50 10.74 8.16 redish yellow 405.44 62.10 3.60 10.20 7.80 yellow 405.44 62.10 3.60 10.20 7.80 15c 188–19	ITa	red	378.37	57.30	2.60	14.79	8.40
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	11b	125 (d)	$C_{19}H_{12}O_4S^{e}$	58.16	3.08	14.27	8.17
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		red	392.40	58.10	3.20	14.10	8.40
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	11c	133 (d)	C ₁₈ H ₉ CIN ₄ O ₄ S ^e	52.37	2.20	13.57	7.77
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	120			52.20	2.30	13.50	7.60
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	12d	152 (u) red	425.26	50.84	2.37	13.17	
	13a	186–188	C10H10N2O1Sa	61.70	2.88	8.00	9.15
13b 172-174 C ₁ H ₁ , ClN, O ₁ S ^a 62.62 3.31 7.69 8.86 pale yellow 364.38 62.50 3.40 7.50 8.70 13c 178-180 C ₁₇ H ₃ N ₂ ClO,S ^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 ₁ N ₂ O ₄ Se ^a 54.42 2.54 7.05 pale yellow 397.25 54.40 2.40 7.10 15 171-173 C ₂₁ H ₁₈ N ₃ O ₄ S ^a 62.21 3.73 10.36 7.90 yellow 405.44 62.21 3.73 10.36 7.90 yellow 405.44 62.10 3.60 10.20 7.83 pale yellow 405.44 62.10 3.60 10.20 7.83 pale yellow 405.44 62.10 3.60 10.20 7.83 f pale yellow 435.30 54.80 3.00 9.50 171		golden yellow	່ຶ35 ັ 0.3້5໋	61.60	2.70	7.90	9.00
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	13b	172–174	$C_{19}H_{12}CIN_2O_4S^a$	62.62	3.31	7.69	8.80
13c 178-180 $C_{18}H_{19}N_2CIO_5S^a$ 56.19 2.36 7.28 8.33 pale yellow 384.80 56.30 2.20 7.20 8.20 14a 185-187 $C_{18}H_{19}N_2O_5S^a$ 54.42 2.54 7.05 pale yellow 397.25 54.40 2.40 7.10 15a 183-185 $C_{20}H_{13}N_2O_5S^a$ 61.37 3.35 10.74 8.15 redish yellow 391.41 61.30 3.50 10.60 8.20 15b 171-173 $C_{21}H_{18}N_3O_4S^a$ 62.21 3.73 10.36 7.90 yellow 405.44 62.10 3.60 10.20 7.80 15c 188-190 $C_{20}H_2(N_3O_5S^a)$ 56.41 2.84 9.87 7.55 pale yellow 438.30 54.80 3.00 9.59 9.59 9.59 17a 263-265 $C_{24}H_{17}N_3O_4S^a$ 66.20 3.50 9.20 7.22 17b 223-225 $C_{28}H_{17}N_3O_4S^a$ 66.80 3.67 8.99 6.86 6.57	40	pale yellow	364.38	62.50	3.40	7.50	8.70
Pate yellow304-00304-0021207.206.2214a165-187 $C_{18}H_{10}N_{0}O_{8}Se^{a}$ 54.422.547.05pale yellow397.2554.402.407.1015a183-185 $C_{21}H_{15}N_{3}O_{4}S^{a}$ 61.373.3510.748.19redish yellow391.4161.303.5010.608.2215b171-173 $C_{21}H_{15}N_{3}O_{4}S^{a}$ 62.213.7310.367.90yellow405.4462.103.6010.207.8615c188-190 $C_{20}H_{12}CN_{3}O_{4}S^{a}$ 56.412.849.877.53pale yellow425.8656.302.709.807.6016a195-197 $C_{20}H_{19}N_{2}O_{5}S^{a}$ 54.812.999.59pale yellow438.3054.803.009.507.2017a263-265 $C_{28}H_{17}N_{2}O_{5}S^{a}$ 66.223.339.277.07orange453.4866.203.509.207.2017b223-225 $C_{28}H_{17}N_{2}O_{5}S^{a}$ 61.532.898.616.57greenish yellow467.5166.703.808.906.9017c251-253 $C_{25}H_{16}N_{2}O_{4}S^{a}$ 61.402.908.606.5018a265-267 $C_{28}H_{16}N_{2}O_{4}S^{a}$ 60.013.028.4062.019173-175 ¹²³ $C_{12}H_{10}N_{2}O_{4}S^{a}$ 69.202.504.7025308-310	13C	178–180 nalo vollow	C ₁₈ H ₉ N₂CIO₄Sª 294.90	56.19	2.36	7.28	8.33
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	14a	185–187	C. H. N.O. Se ^a	54 42	2.20	7.20	0.20
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	114	pale yellow	397.25	54.40	2.40	7.10	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	15a	183–185	$C_{20}H_{13}N_{3}O_{4}S^{a}$	61.37	3.35	10.74	8.19
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		redish yellow	391.41	61.30	3.50	10.60	8.20
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	15b	171–173	$C_{21}H_{15}N_{3}O_{4}S^{a}$	62.21	3.73	10.36	7.90
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	150	188_190	405.44 C H CIN O Sª	62.10 56.41	3.60	9.87	7.80
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	150	pale vellow	425.86	56.30	2.70	9.80	7.60
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	16a	195–197	C ₂₀ H ₁₃ N ₃ O₄Se ^a	54.81	2.99	9.59	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		pale yellow	438.30	54.80	3.00	9.50	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	17a	263–265	$C_{25}H_{15}N_3O_4S^{\circ}$	66.22	3.33	9.27	7.07
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	17h	orange	453.48 CHNOSª	66.20	3.50	9.20	7.20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	175	areenish vellow	467 51	66 70	3.80	8.99	6.90
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	17c	251–253	C₂₅H₁₄CIN₃O₄S°	61.53	2.89	8.61	6.57
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		yellow	² 487.93	61.40	2.90	8.60	6.50
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	18a	265–267	C ₂₅ H ₁₅ N ₃ O ₄ Se ^a	60.01	3.02	8.40	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40	yellow	500.38	66.10	3.10	8.20	40.07
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	19		U ₁₂ H ₇ NU ₃ S [∞] 245.26	58.77	2.88	5.71	13.07
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	20	123–125	C ₄ ,H ₂ NO ₂ Se ^a	49.33	2.90	4,79	13.10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		pale yellow	292.15	49.20	2.50	4.70	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	25	308–310	$C_{19}H_9N_3O_4S^{\circ}$	60.80	2.42	11.19	8.54
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	00	golden yellow	375.37	60.80	2.30	11.10	8.60
pale yellow422.2054.202.209.90 29a 291–293 $C_{18}H_{12}N_4O_2S^d$ 62.063.4716.089.20red348.3962.203.4016.109.20	26	300–302 polo vollovi		54.04	2.15	9.95	
red 348.39 62.20 3.40 16.10 9.20	29a	201_202		04.∠U 62.06	2.20	9.90 16.08	Q 20
		red	348.39	62.20	3.40	16.10	9.20

TABLE 1 Characterization Data of the Newly Synthesized Compounds

% Analyses. Calcd./Found						
Compd	M.p. (°C) Color	Mol. Formula Mol. Wt.	С	Н	Ν	S
29b	296–298	C ₁₉ H ₁₄ N₄O₂S ^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 CIN ₄ O ₂ S ^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 ₄ O ₂ S ^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 N₂O₂S⁰	67.48	3.78	8.74	10.01
	greenish vellow	320.37	67.50	3.70	8.70	10.20
35a	185–186	C ₂₄ H ₁₅ N ₃ O ₃ S⁰	67.75	3.55	9.88	7.54
	vellow	425.47	67.70	3.60	9.80	7.40
35b	202–204	C ₂₄ H ₁₆ N ₄ O ₃ S ^a	65.44	3.66	12.72	7.28
	dark brown	440.48	65.30	3.60	12.90	7.10

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

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 (9ac), 2,3-Dihydroselenadiazole (10a), 2,3-Dihydrothiadiazolo[3,2-a]quinazolinone (25), and 2,3-Dihydroselenadiazolo[3,2a]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 $3-(\omega-\text{thiocyanatoacetyl})$ coumarin 19 or $3-(\omega-\text{selenocyanatoacetyl})$ 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

Compd.	<i>IR</i> (<i>cm</i> ⁻¹)	$^{1}HNMR$ (δ)
3a	3240 (NH), 1724, 1658 (CO's)	7.12–7.97(m, 10H, ArH's and coumarin H-4) and 8.56(s,
3b	3238 (NH), 1732, 1655 (CO's), and 1610 (NH).	2.45(s, 3H, 4-CH ₃ C ₆ H ₄), 7.12–7.97(m, 9H, ArH's and course in 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 ₃ C ₆ H₄), 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 ₃ C ₆ H 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, CH₃CON =), 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 ₃ CON=), 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 ₃ C ₆ H 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, ÁrH's), 8.30(s, 1H, coumarin H-4), and 9.22(s, 1H, NH).

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

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 $3-(\omega$ -Thiocyanatoacetyl)coumarin (19) or $3-(\omega$ -Selenocyanato)acetylcoumarin (20)

A mixture of equimolar quantities of $3-(\omega$ -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 $3-(\omega$ -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).

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