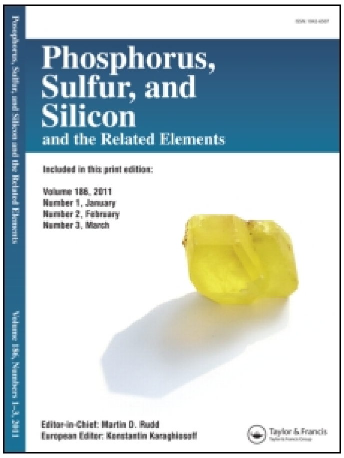

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REACTIONS WITH HYDRAZONOYL HALIDES XXVI [1]:SYNTHESIS AND UTILITY OF C-PYRAZOLOYL-N-ARYLHYDRAZONOYLBROMIDES

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REACTIONS WITH HYDRAZONOYL HALIDES XXVI [1]: SYNTHESIS AND UTILITY OF C-PYRAZOLOYL-N-ARYLHYDRAZONOYL BROMIDES

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2-Arylhydrazono-2-bromo-1-[3-ethoxycarbonyl-5-methyl-1-p-tolyl]pyrazol-4-ylethanone (**5a-e**) were synthesized via reaction of [3-(ethoxycarbonyl-5-methyl-1-p-tolypyrazol-4-oyl]-2-oxoethyl(dimethyl)sulfonium bromide with N-nitrosoacetarylamides in ethanol. The reactions of hydrazonoyl bromides with each of potassium thiocyanate, thiourea, and alkyl carbodithioates are discussed. Structures of the newly synthesized compounds were elucidated on the bases of spectral data, elemental analyses, and alternative method whenever possible.

Keywords: Hydrazonoyl halides; Nitrile imides; 2,3-Dihydrothiadiazoles; Thiazole; thiadiazolo[3,2-a]quinoxazolinone

Hydrazonoyl halides have been largely employed as a exceedingly successful tool for synthesis of heterocyclic compounds[2–6]. In this paper, we reported the synthesis of C-pyrazoloyl-N-arylhydrazonoyl bromides and their reactions towards potassium thiocyanate, thiourea, and alkyl carbodithioates.

Treatment of [3-(ethoxycarbonyl-5-methyl-1-p-tolypyrazol-4-oyl]-2-oxoethyl(dimethyl)sulfonium bromide[7] **2** with the appropriate N-nitrosoacetarylamides **3a-e** in ethanol gave yellow solids. Analytical, spectroscopic data, and their reactions established the structure of the products. IR (cm^{-1}) spectra revealed bands near 3350–3340 (NH), 1740–

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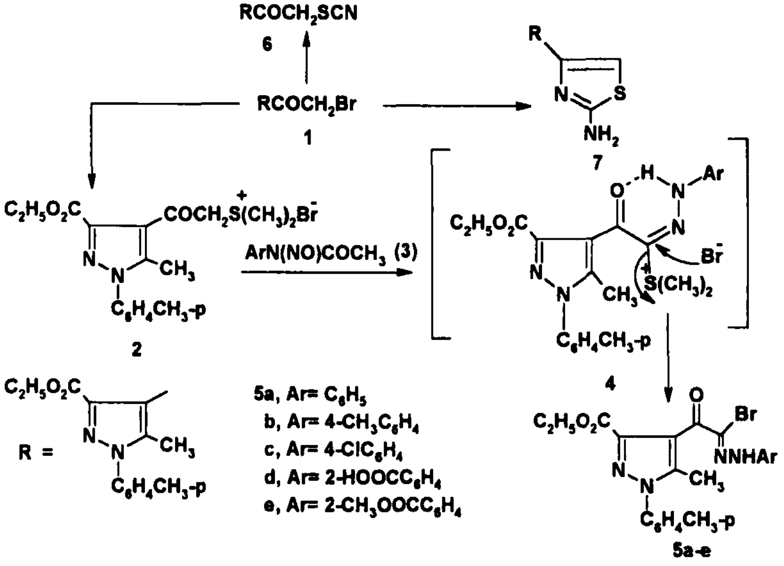
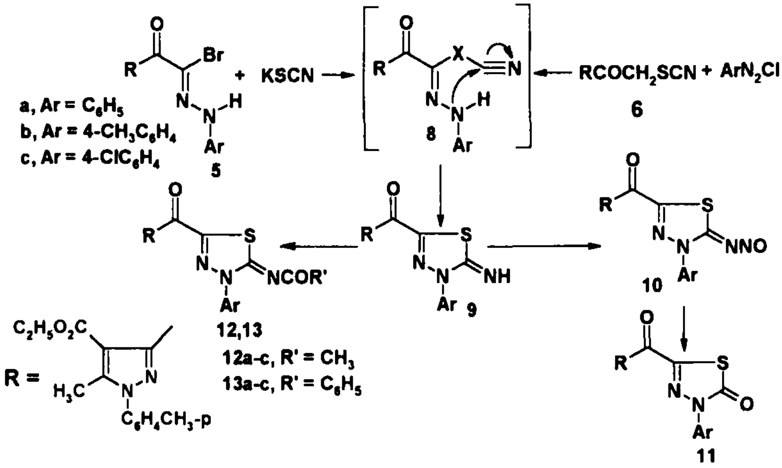
1720 (CO ester) and 1685–1660 (CO conjugated). ^{1}H NMR spectrum of the product (Ar = 4-$CH_3C_6H_4$) showed signals at $\delta = 1.50$(t, 3H, CH_2CH_3); 2.29(s, 3H, CH_3); 2.38(s, 3H, CH_3); 2.43(s, 3H, CH_3); 4.11(q, 2H, CH_2CH_3); 6.97–7.40(m, 8H, ArH's) and 8.54(s, br., 1H, NH). Thus, the products were formulated as: 2-arylhydrazono-2-bromo-1-[3-ethoxy-carbonyl-5-methyl-1-p-tolyl]pyrazol-4-ylethanone (**5a-e**). The probable mechanism that accounts for the foregoing results is presented in Scheme 1. It is assumed that, the intermediate **4** is stabilized in non-aqueous media by interamolecular hydrogen bonding. The nucleophilic attack by the bromide ion produces **5**.



SCHEME 1

Treatment of **5a** with potassium thiocyanate in ethanol at room temperature gave one product identified as: 2-imino-3-phenyl-5-[3′-ethoxycabonyl-5′-methyl-1′-p-tolyl]pyrazol-4′-oyl-2,3-dihydro-1,3,4-thiadiazole (**9a**). Its structure deduced from its spectrum and its chemical reactions described below. IR (cm^{-1}) spectrum of **9a** revealed no band at 2000–2200 due to free -SCN group[8]. The spectrum showed, however, bands at 3306 due to an imino (NH) group, 1735, 1653(2 CO) and 1618(C=N) a moiety. Its ^{1}H NMR spectrum showed signals at 1.20(t, 3H, CH_2CH_3); 2.43(s, 3H,

CH_3); 2.40(s, 3H, CH_3); 4.19(q, 2H, CH_2CH3) and 7.20–7.59(m, 10H, ArH's and NH). Upon shaking with D_2O a new singlet appeared at 4.38 assignable to DOH proton resonance and signal at 7.19–7.85(m, 9H, ArH's). Structure **9a** was further confirmed by independent synthesis. Thus, treatment of 3-ethoxycarbonyl-5-methyl-1-p-tolylpyrazol-4-oylacetylthiocyanate (**6**) with benzenediazonium chloride in ethanolic sodium acetate solution produced a product that proved to be identical in all respects (mp., mixed mp. and spectra) with **9a** prepared above. These results indicated that both the azo coupling of **6** and the reaction of **5a** with potassium thiocyanate proceed through one common intermediate. The latter is undoubtedly the hydrazone **8**, which cyclises readily under the reaction conditions to give **9a** (cf. Scheme 2). Similarly, the reaction of **5b,c** with potassium thiocyanate in ethanol at room temperature gave **9b,c** respectively.



SCHEME 2

Nitrosation of the imino derivatives **9** gave the N-nitroso derivatives **10**. IR (cm^{-1}) spectra of **10** showed no NH band, but revealed common two bands near 1720, 1646(2 CO) and 1535(NO). The ^1H NMR of **10**a showed signals at $\delta = 1.20$(t, 3H, $CH_2\mathit{CH}_3$); 2.34(s, 3H, CH_3); 2.44(s, 3H, CH_3); 4.19(q, 2H, CH_2CH_3) and 7.20–7.59(m, 9H, ArH's).

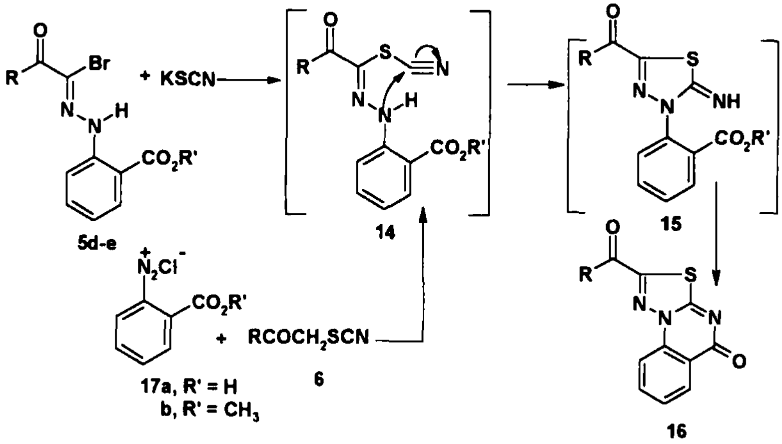
All the compounds **10** decomposed to the corresponding 2,3-dihydro-1,3,4-thiadiazol-2-ones **11** upon refluxing in xylene[9]. The structure of the products **11** was confirmed on the bases of analytical and spectral data studies. IR (cm^{-1}) spectra revealed absorption bands near 1726, 1690 and 1653 (3 CO's). ^1H NMR spectrum of **11b** showed signals at $\delta = 1.59$(t, 3H, $CH_2\mathit{CH_3}$); 2.36(s, 3H, CH_3); 2.39(s, 3H, CH_3); 2.49(s, 3H, CH_3); 4.16(q, 2H, $\mathit{CH_2}CH_3$) and 7.21–7.64(m, 8H, ArH's).

Acylation of **9** with acetic anhydride (and benzoyl chloride in pyridine) afforded the corresponding N-acetyl- (and N-benzoyl-) derivatives **12** and **13**, respectively (cf. Scheme 2). Both elemental analyses and spectral data were consistent with the assigned structures of the products **12** and **13**. The ^1H NMR spectrum of **12b** showed signals at 1.10(t, 3H, $CH_2\mathit{CH_3}$); 2.35(s, 3H, CH_3); 2.40(s, 3H, CH_3); 2.42 (s, 3H, CH_3); 2.44(s, 3H, CH_3); 4.10(q, 2H, $\mathit{CH_2}CH_3$) and 7.26–7.79(m, 8H, ArH's) Its IR (cm^{-1}) spectrum revealed bands at 1727, 1654, 1638 (CO ester, CO conjugated and $CH_3CON=$). ^1H NMR spectrum of **13b** showed signals at 1.10(t, 3H, $CH_2\mathit{CH_3}$); 2.43(s, 3H, CH_3); 2.45(s, 3H, CH_3); 2.46(s, 3H, CH_3); 4.12(q, 2H, $\mathit{CH_2}CH_3$) and 7.25–8.29(m, 13H, ArH's) and its IR (cm^{-1}) spectrum revealed bands at 1740, 1661, 1630 (3 CO's) and 1608 (C=N).

Potassium thiocyanate reacted with hydrazonoyl bromides **5d,e** in ethanol to afford a product having molecular formula $C_{24}H_{19}N_5O_4S$. IR (cm^{-1}) spectrum of the product revealed absorption bands at 1742, 1673, 1639 (3 CO's), and neither absorption bands between 3500–3300 nor 2300–2000 due to NH and SCN. ^1H NMR spectrum showed signals at 1.11(t, 3H, $CH_2\mathit{CH_3}$); 2.44(s, 3H, CH_3); 2.48(s, 3H, CH_3); 4.09(q, 2H, $\mathit{CH_2}CH_3$) and 7.26–8.36(m, 8H, ArH's). From above data the product was formulated as: 2,3-dihydro-2-(3′-ethoxycarbonyl-5′-methyl-1′-p-tolyl) pyrazol-4′-oyl[1,3,4]thiadiazolo[3,2-a]quinoxazolin-9-one (**16**).

On the other hand, treatment of thiocyanate derivative **6** with diazotized anthranilic acid or its methyl ester in ethanolic sodium acetate solution afforded a product identical in all respects (mp., mixed mp. and spectra) with **16**. Scheme 3 shows the possible pathways that account for the formation of **16** from reaction of hydrazonoyl bromide **5d** (or **5e**) with potassium thiocyanate, or coupling of diazotized anthranilic acid or its methyl ester with thiocyanate derivative **6**.

Treatment of **5a** with thiourea in the presence of triethylamine gave a product having the molecular formula $C_{23}H_{22}N_6O_2S$. Its ^1H NMR spectrum showed signals at 1.16(t, 3H, $CH_2\mathit{CH_3}$); 2.39(s, 3H, CH_3); 2.41(s, 3H, CH_3); 4.13(q, 2H, $\mathit{CH_2}CH_3$); 5.93(s, br., 2H, NH_2) and 7.25–7.69(m, 9H, ArH's). Upon shaking with D_2O, the signal at 5.93 disappeared and a

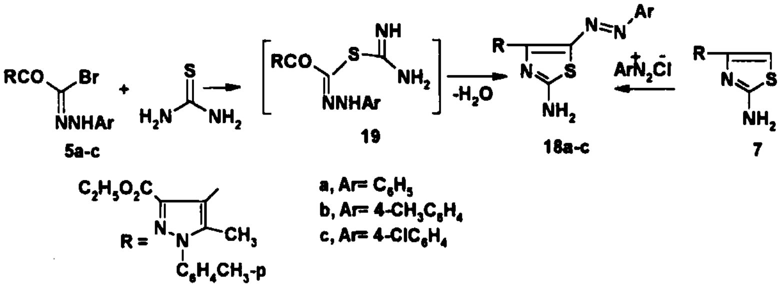


SCHEME 3

new signal at 4.65 appeared due to DOH. Thus the structure was formulated as: 2-amino-5-phenylazo-3-[3′-ethoxycarbonyl-5′-methyl-1′-p-toly] pyrazol-4′-ylthiazole (**18a**) (cf. Scheme 4).

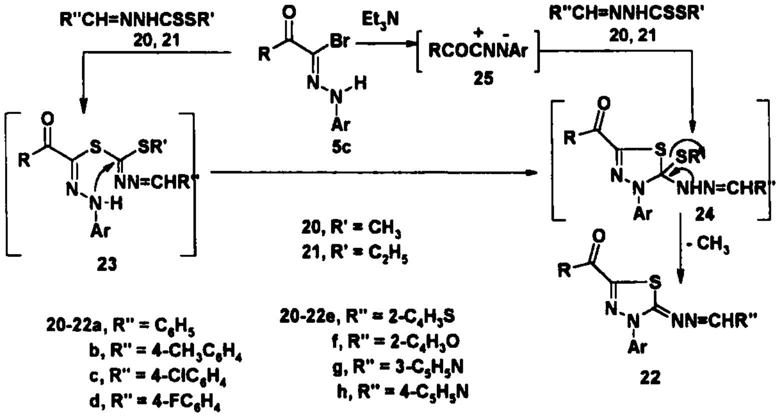
Also, treatment of 2-amino-4-[3′-ethoxycarbonyl-5′-methyl-1-p-tolyl] pyrazol-4′-ylthiazole (7) with benzenediazonium chloride gave a product identical in all respects (mp., mixed mp. and spectra) with **18a**. Scheme 4 shows the possible pathways that account for the formation of **18**. It is assumed that, the first stage involves the formation of a carbon sulfur link by elimination of a molecule of hydrogen bromide to give **19**, by analogy to the reaction of the thioamides with α-halocarbonyl compound [10]. In the second stage, ring closure through direct attack by either the imino or the amino nitrogen atom on the carbonyl carbon and elimination of one molecule of water should give 5-arylazothiazoles **18a-c**.

Finally, the reaction of hydrazonoyl bromide **5c** with the dithioate **20**was studied. Thus, treatment of hydrazonoyl bromide **5c** with the appropriate dithioate **20a** in ethanolic triethylamine solution gave readily the product **22a**. Structure **22** was elucidated on the basis of elemental analysis, spectral data, and alternative synthesis. Thus, IR (cm^{-1}) spectrum of **22a** showed no bands near 3500–3100 corresponding to the NH group. Its ^{1}H NMR (δ ppm) spectrum showed signals at 1.16(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.43(s, 3H, $\mathrm{CH_3}$); 2.45(s, 3H, $\mathrm{CH_3}$); 4.31(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$); 7.26–8.03(m, 13H,



SCHEME 4

ArH's) and 8.41(s, 1H, CH=). Treatment of **5c** with the dithioate **21a** gave a product identical in all respect (mp., mixed mp. and spectra) with compound **22a** (cf. Scheme 5). The formation of **22** can be explained via elimination of methyl mercaptan (or ethyl mercaptan) from the cycloadduct **24**, which is assumed to be formed from the 1,3-dipolar cycloaddition of the nitrile imide **25** to the CS double bond (cf. Scheme 5). Alternatively the formation of the product **25a** can also be explained by a stepwise path involving substitution, to give the acyclic hydrazone **23**, which transferred to the cyclic intermediate **24**. Cyclization of the latter is achieved by elimination of methyl (or ethyl) mercaptan to afford the final isolable product **25a**. All attempts to isolate either the intermediate cycloadduct or the open hydrazone were unsuccessful.



SCHEME 5

Analogy, compounds **20b-h** (or **21b-h**) reacted with the hydrazonoyl bromide **5**c to give the corresponding 2,3-thiadiazoles **22b-h**, respectively.

EXPERIMENTAL

Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. IR (cm^{-1}) spectra were recorded on KBr discs on a FT IR 8201 PC Shimadzu spectrophotometer. ^1H NMR spectra were obtained in $CDCl_3$ or $(CD_3)_2SO$ on a Gemini 200 MHz spectrometer using TMS as an internal reference and chemical shifts were expressed as δ ppm unit. Elemental analyses were performed at the Microanalytical Center, Cairo University. Alkyl carbodithioates[11–13] were prepared as previously reported. Elemental analyses of **16**, **18**a-c and **22**a-c are satisfactory ± 0.2%.

2-Bromo-2-arylhydrazono-1-[3-ethoxycarbonyl-5-methyl-1-p-tolyl]pyrazol-4-ylethanone (5a-e)

A solution of the sulfonium bromide **2** (42.7g, 0.1 mol) and the appropriate N-nitrosoacetarylamides[14–15] (0.15 mol) in ethanol (150 ml) was stirred for 2 hr at room temperature. The reaction mixture was left overnight, then diluted with water (50 ml). The precipitated solid was collected and crystallized from ethanol to give **5a-c** (cf. Tables I and II).

3-Ethoxycarbonyl-5-methyl-1-p-tolylpyrazol-4-oylacetylthiocyanate (6)

A mixture of equimolar quantities of compound **1** and potassium thiocyanate (0.05 mol each), in ethanol (50 ml) was refluxed 30 min. The reaction mixture was cooled the solid, so formed, was collected and then crystallized from ethanol to give **6** (cf. Tables I and II).

2-Amino-4-[3′-ethoxycarbonyl-5′-methyl-1-p-tolyl]pyrazol-4′-ylthiazole (7)

Equimolar amounts of compound **1**{18.25g, 0.05 mol) and thiourea (3.8g, 0.05 mol) in ethanol (50 ml) were refluxed for 2 h and poured onto ice cold water (100 ml) and neutralized with ammonium hydroxide. The resulting solid was collected, washed with water, and crystallized from ethanol to give **7**, in 78% yield (cf. Tables I and II).

TABLE I Characterization data of the newly synthesized compounds

			% Analyses, Calcd. /Found			
Compd no.	*M.P., °C colour*	*Mol.Formula Mol.Wt.*	*C*	*H*	*N*	*S*
5a	152	$C_{22}H_{21}BrN_4O_3$	56.30	4.51	11.94	
	Yellow	469.35	56.50	4.40	12.10	
5b	134–136	$C_{23}H_{23}BrN_4O_3$	57.15	4.80	11.59	
	Yellow	483.37	57.20	4.60	11.70	
5c	195–196	$C_{22}H_{20}BrClN_4O_3$	52.45	4.00	11.12	
	Yellow	503.79	52.60	4.20	11.30	
5d	130–132	$C_{23}H_{21}BrN_4O_5$	53.81	4.12	10.91	
	Yellow	513.36	53.90	4.30	11.10	
5e	150–153	$C_{24}H_{23}BrN_4O_5$	54.66	4.40	10.62	
	Yellow	527.38	54.50	4.60	10.70	
6	88–90	$C_{17}H_{17}N_3O_3S$	59.46	4.99	12.24	9.34
	Yellow	343.41	59.40	4.80	12.30	9.50
7	209–10	$C_{17}H_{18}N_4O_2S$	59.63	5.30	16.36	9.36
	Yellow	342.42	59.50	5.20	16.40	9.50
9a	132–135	$C_{23}H_{21}N_5O_3S$	61.73	4.73	15.65	7.16
	Yellow	447.52	61.90	4.60	15.50	7.00
9b	163–165	$C_{24}H_{23}N_5O_3S$	62.46	5.02	15.17	6.95
	Yellow	461.55	62.60	4.90	14.90	7.10
9c	135–138	$C_{23}H_{20}ClN_5O_3S$	57.32	4.18	14.53	6.65
	Yellow	481.96	57.50	4.30	14.60	6.80
10a	103 dec.	$C_{23}H_{20}N_6O_4S$	57.97	4.23	17.64	6.73
	Red	476.52	57.70	4.30	17.50	6.50
10b	85 dec.	$C_{24}H_{22}N_6O_4S$	58.76	4.52	17.13	6.54
	Red	490.54	58.60	4.40	17.20	6.40
10c	105 dec.	$C_{23}H_{19}ClN_6O_4S$	54.07	3.75	16.45	6.28
	Red	510.96	54.10	3.70	16.50	6.40
11a	148–50	$C_{23}H_{20}N_4O_4S$	61.60	4.49	12.49	7.15

			% Analyses, Calcd. /Found			
Compd no.	*M.P., °C colour*	*Mol.Formula Mol.Wt.*	*C*	*H*	*N*	*S*
	Yellow	448.50	61.50	4.30	12.60	7.30
11b	208–10	$C_{24}H_{22}N_4O_4S$	62.32	4.79	12.11	6.93
	Yellow	462.53	62.20	4.60	12.10	7.10
11c	150	$C_{23}H_{19}ClN_4O_4S$	57.20	3.97	11.60	6.64
	Yellow	482.95	57.10	4.00	11.50	6.40
12a	153–155	$C_{25}H_{23}N_5O_4S$	61.34	4.74	14.31	6.55
	Yellow	489.57	61.40	4.70	14.20	6.50
12b	180–82	$C_{26}H_{25}N_5O_4S$	62.01	5.00	13.90	6.37
	Yellow	503.58	61.90	4.90	13.80	6.50
12c	183–85	$C_{25}H_{22}ClN_5O_4S$	57.30	4.23	13.37	6.12
	Pale yellow	524.00	57.30	4.10	13.50	6.20
13a	217–20	$C_{30}H_{25}N_5O_4S$	65.32	4.57	12.70	5.81
	Yellow	551.63	65.40	4.40	12.60	5.90
13b	207–9	$C_{31}H_{27}N_5O_4S$	65.83	4.81	12.38	5.67
	Yellow	565.66	65.70	5.00	12.40	5.80
13c	148–50	$C_{30}H_{24}ClN_5O_4S$	61.48	4.13	11.95	5.47
	Yellow	586.07	61.60	4.20	12.10	5.60
22d	170–72	$C_{30}H_{24}ClFN_6O_3S$	59.75	4.01	13.94	5.32
	Yellow	603.08	59.80	3.90	13.80	5.20
22e	205–207	$C_{28}H_{23}ClN_6O_3S_2$	56.89	3.92	14.22	10.85
	Yellow	591.11	56.90	4.00	14.10	10.60
22f	188–90	$C_{28}H_{23}ClN_6O_4S$	58.48	4.03	14.61	5.58
	Yellow	575.05	58.50	4.10	14.80	5.40
22g	185–6	$C_{29}H_{24}ClN_7O_3S$	59.43	4.134.	16.73	5.47
	Yellow	586.08	59.30	20	16.70	5.47
22h	204–5	$C_{29}H_{24}ClN_7O_3S$	59.43	4.13	16.74	5.47
	Yellow	586.08	59.30	4.00	16.60	5.60

IR (cm^{-1})	^{1}H NMR (δ ppm)
53(NH); 1728, 1649(CO's)	1.48(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.29(s, 3H, CH_3); 2.38(s, 3H, CH_3); 4.11(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$); 6.97–7.40(m, 9H, Ar and 8.54(s, br., 1H, NH).
40(NH); 1716, 1656(CO's)	1.49(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.29(s, 3H, CH_3); 2.38(s, 3H, CH_3); 4.13(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$); 6.97–7.40(m, 8H, Ar and 8.53(s, br., 1H, NH).
50–2613 (OH, NH); 1724, 0, 1650(CO's)	1.48(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.29(s, 3H, CH_3); 2.38(s, 3H,, CH_3); 4.12(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$); 6.97–7.98(m, 8H, Ar 11.6(s, 1H, COOH) and 11.98(s, br., 1H, NH).
3(NH), 1723, 1685(CO's).	1.50(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.29(s, 3H, CH_3); 2.38(s, 3H,, CH_3); 3.96(s, 3H, OCH_3); 4.07(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$); 6.97–7.98(m, 8H, ArH's), and 11.98(s, br., 1H, NH).
5(SCN); 1728, 1678(CO's).	1.41(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.42(s, 6H, $2CH_3$); 4.45(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$); 4.66(s, 2H, CH_2); 7.26–7.29(m, 4H, A
7; 3146(NH2); 1728(CO).	1.31(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.32(s, 3H, CH_3); 2.40(s, 3H, CH_3); 4.33(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$); 5.12(s, 2H, NH_2) 6.73 thiazole H-5) and 7.21–7.35(m, 4H, ArH's).
5(NH); 1730, 1660(CO's).	1.21(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.34(s, 3H, CH_3); 2.40(s, 3H,, CH_3); 4.11(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$); 7.20–7.55(m, 9H, Ar and NH).
0, 1649(CO's); 1430(N=O).	1.16(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.36(s, 3H, CH_3); 2.39(s, 3H, CH_3); 2.49(s, 3H, CH_3); 4.16(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$) and 7.21–7.64(m, 8H, ArH's).
0, 1649(CO's); 1435(N=O).	1.16(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.36(s, 3H, CH_3); 2.39(s, 3H, CH_3); 4.16(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$) and 7.21–7.64(m, 8H, A
6, 1690, 1653 (CO's).	1.59(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.36(s, 3H, CH_3); 2.39(s, 3H, CH_3); 4.16(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$) and 7.21–7.64(m, 9H, A
6, 1690, 1653 (CO's).	1.59(t, 3H, $\mathrm{CH_2}\mathit{CH_3}$); 2.36(s, 3H, CH_3); 2.39(s, 3H, CH_3); 4.16(q, 2H, $\mathit{CH_2}\mathrm{CH_3}$) and 7.21–7.64(m, 8H, A

IR (cm^{-1})	*^{1}H NMR (δ ppm)*
7, 1654, 1638 (CO's).	1.10(t, 3H, CH_2CH_3); 2.35(s, 3H, CH_3); 2.40(s, 3H, CH_3); 2.42(s, 3H, CH_3); 4.10(q, 2H, CH_2CH_3) and 7.26–7.79(m, 9H, ArH's).
0, 1661, 1630 (CO's).	1.10(t, 3H, CH_2CH_3); 2.45(s, 3H, CH_3); 2.46(s, 3H, CH_3); 4.10(q, 2H, CH_2CH_3) and 7.26–8.29(m, 14H ArH's).
0, 1661, 1630 (CO's).	1.10(t, 3H, CH_2CH_3); 2.45(s, 3H, CH_3); 2.46(s, 3H, CH_3); 4.10(q, 2H, CH_2CH_3) and 7.26–8.29(m, 13H ArH's).
9, 3117(NH_2); 1720(CO).	1.16(t, 3H, CH_2CH_3); 2.39(s, 3H, CH_3); 2.41(s, 3H, CH_3); 4.19(q, 2H, CH_2CH_3); 5.93(s, 2H, NH_2) and 7.25–7.69(m, 9H, ArH's)
9, 3117(NH_2); 1720(CO).	1.16(t, 3H, CH_2CH_3); 2.39(s, 3H, CH_3); 2.41(s, 3H, CH_3); 2.43(s, 3H, CH_3); 4.19(q, 2H, CH_2CH_3); 5.93(NH_2) and 7.25–7.69(m, 8H, ArH's).
9, 3117(NH_2); 1720(CO).	1.16(t, 3H, CH_2CH_3); 2.39(s, 3H, CH_3); 2.41(s, 3H, CH_3); 4.19(q, 2H, CH_2CH_3); 5.93(s, 2H, NH_2) and 7.25–7.69(m, 8H, ArH's).
2, 1656(CO's)	1.16(t, 3H, CH_2CH_3); 2.43(s, 3H, CH_3); 2.45(s, 3H, CH_3); 4.15(q, 2H, CH_2CH_3); 7.21–8.03(m, 13H, Ar and 8.41(s, 1H, CH).

2,3-Dihydro-1,3,4-thidiazoles 9a-c and 5-arylazothiazoles 18a-c

Method (A)

To a solution of potassium thiocyanate or thiourea (0.005 mol) in ethanol (30 ml), a solution of the appropriate of hydrazonoyl bromide **5a-c** (0.005 mol) was added with stirring. The reaction mixture was stirred for 4 h at room temperature. During this period, the material went into solution and new solid precipitated. The latter was collected, washed with water, and crystallized from ethanol. Compounds **9a-c** and **18a-c** prepared are listed with their physical constants in Tables I and II. **8a**, m.p. 250-51, **18b**, m.p. 240-41 and **18c**, m.p. 259-60°C.

Method (B)

A cold solution of the appropriate thiocanate 6 or thiazole 7 (0.01 mol) and sodium acetate trihydrate (1.3g, 0.01 mol) in ethanol (50 ml) was treated, while stirring, with the appropriate diazotized primary aromatic amines (0.01 mol) and left in the ice chest for 8 h. The solid formed was collected, washed with water, and then crystallized from ethanol. All compounds prepared by this method are identical in all respects (m.p., mixed m.p. and spectra) with those prepared above.

N-Nitrosoimino-Δ^2-1,3,4-thiadiazoline 10a-c

A solution of **9a-c** (1 g) in acetic acid (30 ml) was treated with a saturated solution of sodium nitrite while stirring (30 min.). The reddish product precipitated was collected and crystallized from ethanol. Compounds **10a-c** were obtained in almost quantitative yield (cf. Tables I and II).

1,3,4-Thiadiazolinones 11a-c

The appropriate N-nitroso derivatives **10a-c** (1.0g) were refluxed in xylene (30 ml) for 30 min., the solvent was removed, and little ethanol was added to the residue. The formed precipitate was collected and then crystallized from ethanol. The products **11a-c** with their physical properties are listed in Tables I and II.

Acylation of 9a-c

a) Acetylation: The appropriate compounds **9a-c** (1.0 g) were refluxed in acetic anhydride (10 ml) for 15 min., cooled and poured onto crushed ice (50 g). The crude solid precipitated was collect and crystallized from acetic acid (cf. Tables I and II).

b) Benzoylation: Equimolecular amounts of the appropriate **9a-c** and benzoyl chloride (0.005 mol each) in pyridine (10 ml) were refluxed for 10 min., cooled and poured onto dilute cold hydrochloric acid (6 M, 50 ml). The solid was collected, washed with hot water and then crystallized from acetic acid, to give **13a-c**, respectively in 60–73% yield (cf. Tables I and II).

Thiadiazolo[3,2-a]quinazolin-9-one 16

Method (A)

To a cold solution of thiocyanate 6 (3.4g, 0.01 mol) and sodium acetate (1.3g) in ethanol (50 ml) was added, dropwise a solution of diazotized anthranilic acid (or its methyl ester) (0.01 mol) while stirring. The addition took 30 minutes, after which stirring was continued for 30 minutes. The solid formed was collected, washed with water, and finally crystallized from acetic acid to give **16** m.p. 210°C.

Method (B)

To a suspension of the appropriate hydrazonoyl bromide 5d or 5e (5 mmol) in ethanol (20 ml), a solution of potassium thiocyanate (1g, 10 mmol) in water (5 ml) was added. The reaction mixture was stirred for 24 h. at room temperature. The crude product formed was collected, washed with water and crystallized from acetic acid. The product obtained from **5d** and **5e** were identical in all respects with each other (mp., mixed mp., and spectra).

2,3-Dihydrothiadiazoles 22a-h

General Procedure

To a solution of the appropriate dithiocarbazate[125–127] 20a-h(or 21a-h and hydrazonoyl bromide **5c** (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 h, and the solid which formed was collected, washed with water and crystallized from acetic acid to give **22a-h**, respectively (cf. Tables I and II). **22a**, m.p. 190-2, **22b**, m.p. 202-4 and **22c**, m.p. 191-3°C.

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