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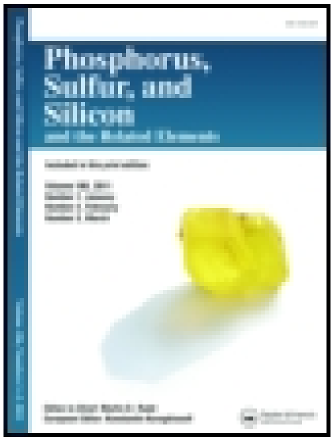

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Reactions with Hydrazonoyl Halides 34[1]: Synthesis of Some New 2,3-Dihydro-1,3,4-thiadiazoles

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REACTIONS WITH HYDRAZONOYL HALIDES 34[1]: SYNTHESIS OF SOME NEW 2,3-DIHYDRO-1,3,4-THIADIAZOLES

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*Hydrazonoyl halides **4a–h** have been caused to react with each of alkyl carbodithioates (**3**, **13–17**)**a**,**b** in the presence of triethylamine to give 2,3-dihydro-1,3,4-thiadiazoles in good yields. Structures of the new compounds were elucidated on the basis of elemental analyses, spectral data, and alternative methods of synthesis whenever possible.*

Keywords: 1,3-dipolar cycloaddition; 1,3,4-thiadiazoles; carbodithioates; hydrazonoyl halides; unsymmetrical azines

1,3,4-Thiadiazole and its derivatives have become very useful compound in medicine, agriculture and in many fields of technology.[2] Although few patented compounds become marketed products, patents do give a rough indication of utility. Some of the technological uses involve dyes, lubricant compositions, optically active liquid crystals, photographic materials, epoxy resins and miner others. A large number of thiadiazoles have been patented in the agricultural filed as herbicides, insecticides, fungicides, bactericides, and anthelmintics. In the medical field they have been patents for almost every disease known to man, and quite a few of them have become commercial products. As an extension of our study[3–5] and as a part of our program aiming at the synthesis of different 1,3,4-thiadiazoles, here we report on the reactivity of α-keto hydrazonoyl halides toward some alkyl carbodithioates.

RESULTS AND DISCUSSION

The reaction of equimolar amounts of *C*-ethoxycarbonyl-*N*-phenylhydrazonoyl chloride (**4a**) with [((1E,3E)-1-aza-4-phenylbuta-1,3-dienyl)amino]methylthiomethane-1-thione (**3a**) in ethanolic

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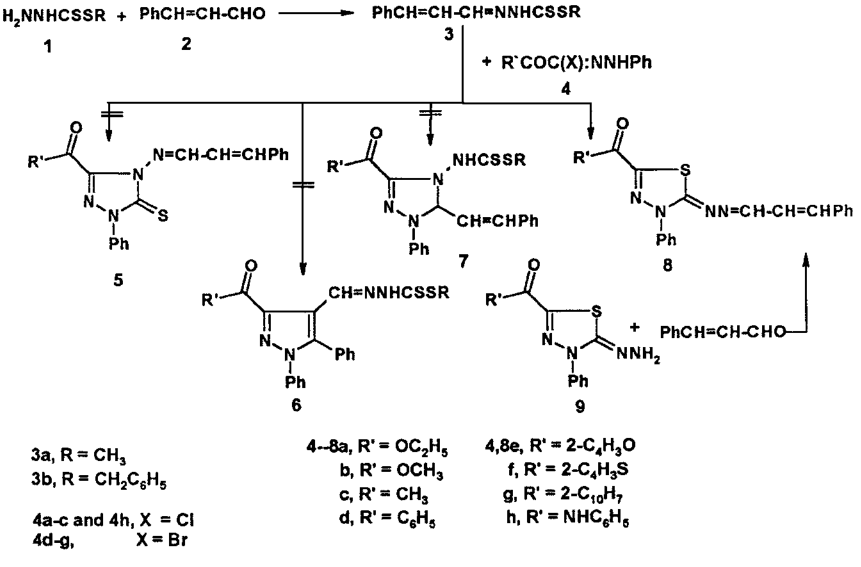
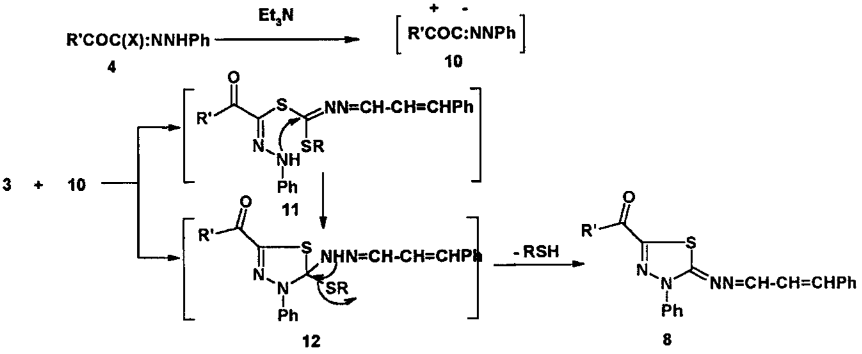
triethylamine solution furnished exclusively one product (as evidenced by TLC) and its structure is seemed to be **5–8**. Elemental analyses, spectral data, and alternative synthesis are in agreement with the formation of ethyl 2-((2E,4E)-1,2-diaza-5-phenylpenta-2,4-dienylidene)-3-phenyl-1,3,4-thiadiazoline-5-carboxylate (**8a**). Thus, the IR (cm^{-1}) spectrum of the product revealed bands at 1710 (CO), 1618 (C=N) and 1583 (C=C). Its ^{1}H NMR (δ ppm) showed signals at δ = 1.42 (t, 3H, CH_2CH_3), 4.47 (q, 2H, CH_2CH_3), 6.95–7.51 (m, 10H, ArH's), 7.96–8.00 (d, 2H), and 8.19–8.23 (d, 1H). Unequivocal support of the structure of **8** obtained by reaction of 2-hydrazino-2,3-dihydro–1,3,4–thiadiazole[6] (**9**) with cinnamaldehyde gave identical product in all respects (m.p., mixed m.p., and spectra) with **8a** (cf. Scheme 1). Also, **4a** reacted with **3b** in ethanolic triethylamine gave product identical in all respects (m.p., mixed m.p., and spectra) with **8a**. Structures **5–7** were excluded on the basis of the previous data.



SCHEME 1

Two possible pathways can account for the formation of **8**: 1) 1,3-Addition of the thiol tautomer **3** to the nitrilium imide **10a**, (which prepared in situ by treatment of hydrazonoyl chloride **4a** with triethylamine), can give the thiohydrazonate ester **11a**, which undergoes nucleophilic cyclization to yield **12a**, which affords **8a** by loss of RSH; and 2) 1,3-cycloaddition of the nitrilium imide **10a** to the C=S of **3a** (or **3b**) can give **12a** directly (cf. Scheme 2).



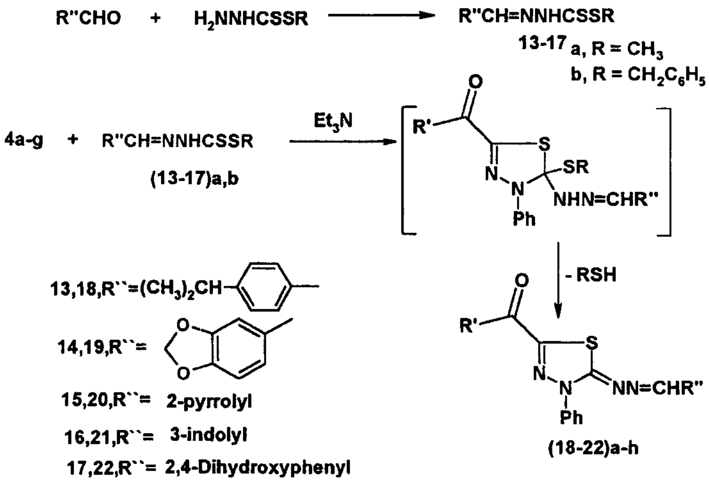
SCHEME 2

Similarly, the appropriate hydrazonoyl halides **4b–h** react with each of alkyl carbodithioate **3a** (or **3b**), to afford 2,3-dihydro-1,3,4-thiadiazole derivatives **8b–h** respectively.

Hydrazonoyl chloride **4a** reacts with the appropriate ({(1E)-1-aza-2-[4-(methylethyl)phenyl]vinyl}amino)methylthiomethane-1-thione (**13a**) or (methane{(1E)-1-aza-2-[4-(methylethyl)phenyl]vinyl}amino)-phenylmethylthio-1-thione (**13b**) in ethanolic triethylamine afforded, in each case, the same isolable product (m.p., mixed m.p., and spectra). Structure **18a** was assigned to the isolated products on the bases of their elemental analyses and spectral data. For example, IR spectra of **18a** revealed absorption band at 1710 cm^{-1} due to the carbonyl group. Its ^1H NMR spectrum showed signals at δ_H 1.25 (d, 6H, $2CH_3$), 1.40 (t, 3H, CH_3CH_2), 2.94 (hept., 1H, $CH(CH_3)_2$), 4.45 (q, 2H, CH_2CH_3), 7.25–8.02 (m, 9H, ArH's) and 8.38 (s, 1H, CH).

By similar route, the appropriate alkyl carbodithioates **13** (**a**, **b**) react with the appropriate hydrazonoyl halides **4b–h** to afford unsymmetrical azines **18b–h**, respectively (cf. Scheme 3).

Hydrazonoyl chloride **4a** reacts with each of the appropriate [((1E)-2-(2H-benzo[3,4-d]1,3-dioxolan-5-yl)-1-azavinyl)amino]methylthiomethane-1-thione (**14a**), [((1E)-2-(2H-benzo[3,4-d]1,3-dioxolan-5-yl)-1-azavinyl)amino](phenylmethylthio)methane-1-thione (**14b**), [((1E)-1-aza-2-pyrol-2-ylvinyl)amino]methylthiomethane-1-thione (**15a**), [((1E)-1-aza-2-pyrrol-2-ylvinyl)amino]phenylmethylthio)methane-1-thione (**15b**), [((1E)-1-aza-2-indol-3-ylvinyl)amino]methylthiomethane-1-thione (**16a**), [((1E)-1-aza-2-indol-3-ylvinyl)amino]phenylmethylthio)methane-1-thione (**16b**), 4-{(1E)-2-aza-2-[(methylthiothioxomethyl)-amino]vinyl}benzene-1,2-diol (**17a**), 4-{(1E)-2-aza-2-[(phenylmethylthio)thioxomethyl)-amino]vinyl}benzene-1,2-diol (**17b**), to give 2,3-dihydro-1,3,4-thiadiazoles (**19–22**)**a** respectively. Structures

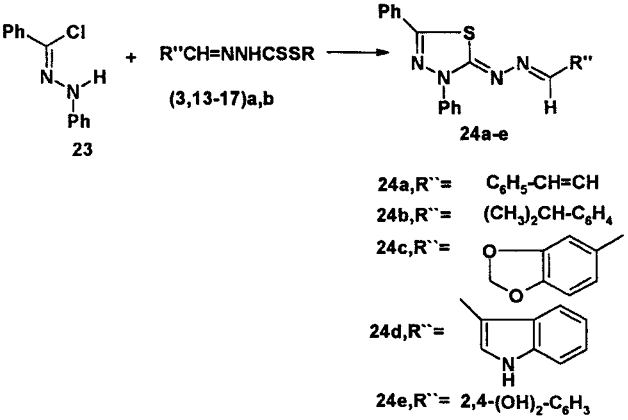


SCHEME 3

19–22 were confirmed on the basis of elemental analyses, spectral data, and alternative synthesis (cf. Scheme 3 and Experimental).

Analogously, the appropriate hydrazonoyl halides **4b–h**, react with the appropriate (**14–17**)**a**,**b** in ethanol containing triethylamine at room temperature to give unsymmetrical azines (**18–22**)**b–h**, respectively, in a good yields.

Moreover, *C*-phenyl-*N*-phenylhydrazonoyl chloride (**23**) reacts with the appropriate methyl carbodithioates (**3**, **13–17**)**a**, in ethanolic trietyhlamine to give the corresponding 2,3-dihydro-1,3,4-thiadiazoles **24a–e**, respectively (cf. Scheme 4).



SCHEME 4

TABLE I Characterization Data of the Newly Synthesized Compounds

Compd. no.	m.p., °C solvent	Yield (%)	Mol. formula (mol. wt.)	% Analyses, calcd./found			
				C	H	N	S
3a	160–162	89	$C_{11}H_{12}N_2S_2$	55.90	5.12	11.85	27.13
	EtOH		(236.36)	56.20	5.30	12.00	27.30
3b	187–189	87	$C_{17}H_{16}N_2S_2$	65.35	5.16	8.97	20.52
	EtOH		(312.46)	65.50	5.30	9.00	20.70
8a	118–120	85	$C_{20}H_{18}N_4O_2S$	63.47	4.79	14.80	8.47
	EtOH		(378.46)	63.60	4.90	15.00	8.60
8b	135–138	87	$C_{19}H_{16}N_4O_2S$	62.62	4.43	15.37	8.80
	ACOH		(364.43)	62.40	4.40	15.10	8.60
8c	160–162	87	$C_{19}H_{16}N_4OS$	65.50	4.63	16.08	9.20
	ACOH		(348.43)	65.30	4.40	15.90	9.00
8d	175–176	90	$C_{24}H_{18}N_4OS$	70.22	4.42	13.65	7.81
	ACOH		(410.50)	70.40	4.60	13.80	8.00
8e	190–191	80	$C_{22}H_{16}N_4O_2S$	65.99	4.03	13.99	8.01
	ACOH		(400.46)	66.00	4.20	14.00	8.20
8f	198–200	78	$C_{22}H_{16}N_4OS_2$	63.45	3.87	13.45	15.40
	ACOH		(416.46)	63.20	3.60	13.20	15.10
8g	168–170	75	$C_{28}H_{20}N_4OS$	73.02	4.38	12.16	6.96
	ACOH		(460.56)	73.00	4.30	12.10	6.90
8h	200–202	78	$C_{24}H_{19}N_5OS$	67.75	4.50	16.46	7.54
	ACOH		(425.49)	67.50	4.30	16.20	7.20
13a	106–108	80	$C_{12}H_{16}N_2S_2$	57.10	6.39	11.10	25.41
	EtOH		(252.40)	57.30	6.50	11.30	25.60
13b	65–67	55	$C_{18}H_{20}N_2S_2$	65.81	6.14	8.53	19.52
	EtOH		(328.50)	66.00	6.30	8.70	19.70
14a	199–200	90	$C_{10}H_{10}N_2O_2S_2$	47.00	3.92	11.01	25.21
	EtOH		(254.33)	47.20	4.10	11.20	25.40
14b	180–182	95	$C_{16}H_{14}N_2O_2S_2$	58.16	4.27	8.48	19.41
	ACOH		(330.43)	58.30	4.40	8.60	19.60
15a	124–124	95	$C_7H_9N_3S_2$	42.19	4.55	21.08	32.18
	EtOH		(199.30)	42.40	4.80	21.30	32.30
15b	130–133	90	$C_{13}H_{13}N_3S_2$	56.70	4.76	15.26	23.29
	EtOH		(275.40)	56.90	4.90	15.40	23.40
16a	193–196	95	$C_{11}H_{11}N_3S_2$	52.99	4.45	16.85	25.72
	EtOH		(249.36)	53.10	4.60	17.00	25.90
16b	188–190	91	$C_{17}H_{15}N_3S_2$	62.74	4.65	12.91	19.70
	EtOH		(325.46)	62.50	4.40	12.70	19.50
17a	207–210	86	$C_9H_{10}N_2O_2S_2$	44.61	4.16	11.56	26.46
	EtOH		(242.32)	44.80	4.30	11.70	26.60
17b	175–177	85	$C_{15}H_{14}N_2O_2S_2$	56.58	4.43	8.80	20.14
	EtOH		(318.42)	56.80	4.30	8.90	19.80
18a	85–86	85	$C_{21}H_{22}N_4O_2S$	63.94	5.62	14.20	8.13
	EtOH		(394.50)	64.00	5.80	14.40	8.30
18b	98–100	75	$C_{20}H_{20}N_4O_2S$	63.14	5.30	14.73	8.43
	EtOH		(380.47)	63.30	5.50	14.90	8.60
18c	134–135	87	$C_{20}H_{20}N_4OS$	65.91	5.53	15.37	8.80
	ACOH		(364.47)	65.70	5.30	15.10	8.60

(Continued on next page)

TABLE I Characterization Data of the Newly Synthesized Compounds (*Continued*)

Compd. no.	m.p., °C Solvent	Yield (%)	Mol. formula (mol. wt.)	% Analyses, calcd./found			
				C	H	N	S
18d	145–147	89	$C_{25}H_{22}N_4OS$	70.40	5.20	13.14	7.52
	ACOH		(426.54)	70.60	5.50	13.30	7.70
18e	163–165	85	$C_{23}H_{20}N_4O_2S$	66.33	4.84	13.45	7.60
	ACOH		(416.51)	66.10	4.60	13.10	7.40
18f	183–184	79	$C_{23}H_{20}N_4OS_2$	63.86	4.66	12.95	14.82
	ACOH		(432.56)	63.80	4.60	12.90	14.80
18g	138–140	81	$C_{29}H_{24}N_4OS$	73.08	5.08	11.76	6.73
	ACOH		(476.60)	73.30	5.20	11.80	6.90
18h	133–135	83	$C_{25}H_{23}N_5OS$	68.00	5.25	15.86	7.26
	ACOH		(441.56)	68.20	5.40	16.00	7.40
19a	180–182	80	$C_{19}H_{16}N_4O_4S$	57.57	4.07	14.13	8.09
	EtOH		(396.43)	57.80	4.00	14.30	8.30
19b	173–175	93	$C_{18}H_{14}N_4O_4S$	56.54	3.69	14.65	8.34
	ACOH		(382.40)	56.70	3.90	14.90	8.50
19c	162–163	83	$C_{18}H_{14}N_4O_3S$	59.01	3.85	15.29	8.75
	ACOH		(366.40)	59.30	4.00	15.40	8.90
19d	166–168	86	$C_{23}H_{16}N_4O_3S$	64.47	3.76	13.08	7.48
	ACOH		(428.47)	64.40	3.70	13.00	7.40
19e	243–245	80	$C_{21}H_{14}N_4O_4S$	60.25	3.37	13.39	7.66
	ACOH		(418.43)	60.40	3.50	13.50	7.80
19f	169–170	85	$C_{21}H_{14}N_4O_3S_2$	58.05	3.25	12.98	14.76
	ACOH		(434.50)	58.30	3.40	13.00	15.00
19g	208–210	89	$C_{27}H_{18}N_4O_3S$	67.77	3.79	11.71	6.70
	ACOH		(478.53)	67.70	3.70	11.60	6.50
19h	170–172	90	$C_{23}H_{17}N_5O_3S$	62.29	3.86	15.79	7.23
	ACOH		(443.49)	62.40	4.00	16.00	7.50
20a	122–124	90	$C_{16}H_{15}N_5O_2S$	56.29	4.43	20.51	9.39
	EtOH		(341.40)	56.10	4.40	20.40	9.30
20b	159–160	84	$C_{15}H_{13}N_5O_2S$	55.04	4.00	21.39	9.79
	EtOH		(327.37)	55.10	4.10	21.50	10.00
20c	173	93	$C_{15}H_{13}N_5OS$	57.86	4.21	22.49	10.30
	EtOH		(311.37)	57.80	4.20	22.40	10.30
20d	149–150	95	$C_{20}H_{15}N_5OS$	64.33	4.05	18.75	8.59
	EtOH		(373.44)	64.30	4.20	18.90	8.70
20f	160	93	$C_{18}H_{13}N_5OS_2$	56.98	3.45	18.46	16.90
	EtOH		(379.47)	67.00	3.40	18.40	16.90
20h	148–150	85	$C_{20}H_{16}N_6OS$	61.84	4.15	21.63	8.25
	EtOH		(388.45)	61.60	4.00	21.40	8.00
21a	218–220	93	$C_{20}H_{17}N_5O_2S$	61.37	4.38	17.89	8.19
	EtOH		(391.45)	61.50	4.50	17.90	8.30
21b	236–236	98	$C_{19}H_{15}N_5O_2S$	60.46	4.01	18.56	8.49
	EtOH		(377.43)	60.40	4.00	18.50	8.50
21c	218–229	95	$C_{19}H_{15}N_5OS$	63.14	4.18	19.38	8.87
	EtOH		(361.43)	63.00	4.00	19.10	8.60

(Continued on next page)

TABLE I Characterization Data of the Newly Synthesized Compounds (*Continued*)

Compd. no.	m.p., °C Solvent	Yield (%)	Mol. formula (mol. wt.)	% Analyses, calcd./found C	H	N	S
21d	248	91	$C_{24}H_{17}N_5OS$	68.07	4.05	16.54	7.57
	ACOH		(423.50)	68.20	4.00	16.70	8.00
21f	305–307	92	$C_{22}H_{15}N_5OS_2$	61.52	3.52	16.30	14.93
	ACOH		(429.53)	61.50	3.50	16.30	15.00
21h	277–280	85	$C_{24}H_{18}N_6OS$	65.74	4.14	19.16	7.31
	ACOH		(438.51)	65.70	4.10	19.10	7.30
22a	200–203	87	$C_{18}H_{16}N_4O_4S$	56.24	4.16	14.57	8.34
	EtOH		(384.42)	56.20	4.20	14.50	8.30
22b	195–198	86	$C_{17}H_{14}N_4O_4S$	55.13	3.81	15.13	8.66
	EtOH		(370.39)	55.10	3.90	15.30	8.60
22c	217	90	$C_{17}H_{14}N_4O_3S$	57.62	3.98	15.81	9.05
	EtOH		(354.39)	57.40	3.70	15.60	9.00
22d	218–220	89	$C_{22}H_{16}N_4O_3S$	63.45	3.87	13.45	7.70
	EtOH		(416.46)	63.60	4.00	13.60	7.90
22f	239–241	92	$C_{20}H_{14}N_4O_3S_2$	56.86	3.34	13.26	15.18
	EtOH		(422.49)	56.80	3.30	13.20	15.10
24a	138–140	85	$C_{23}H_{18}N_4S$	72.23	4.74	14.65	8.38
	EtOH		(382.49)	72.00	4.50	14.40	8.10
24b	113–115	81	$C_{24}H_{22}N_4S$	72.33	5.56	14.06	8.05
	EtOH		(398.53)	72.30	5.50	14.00	8.00
24c	195–197	90	$C_{22}H_{16}N_4O_2S$	65.99	4.03	13.99	8.01
	EtOH		(400.46)	66.00	4.00	14.00	8.00
24d	210–212	85	$C_{23}H_{17}N_5S$	69.84	4.33	17.71	8.11
	EtOH		(395.49)	69.90	4.50	17.90	8.30
24e	235–238	87	$C_{21}H_{16}N_4O_2S$	64.93	4.15	14.42	8.25
	EtOH		(388.45)	64.90	4.10	14.40	8.20

Structure **24** was confirmed on the basis of elemental analyses, spectral data, and alternative route synthesis. Thus, **23** reacted with the appropriate benzyl carbodithioates (**3**, **13–17**)**b** in ethanolic triethylamine at room temperature gave identical product (m.p., mixed m.p., and spectra) with the corresponding **24a–e** which obtained before.

EXPERIMENTAL

All melting points were determined on an Electrothermal apparatus and are uncorrected. IR spectra were recorded (KBr discs) on a Shimadzu FT-IR 8201 PC spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ on a Varian Gemini 200 MHz spectrometer and chemical shifts were expressed in δ units using TMS as internal reference. Elemental analyses were carried out at the

TABLE II ^{1}H NMR Spectra of Some Selected Synthesized Compounds

Compd. no.	^{1}H NMR (δ ppm)
3a	2.66 (s, 3H), 6.94–7.79 (m, 8H) and 10.91 (s, br., 1H).
3b	4.47 (s, 2H), 6.88–8.10 (m, 13H) and 13.2 (s, 1H).
8b	3.92 (s, 3H), 7.95–8.2 (m, 13H).
8c	2.62 (s, 3H), 7.95–7.55 (m, 10H), 7.98–8.02 (d, 2H) and 8.19–8.24 (t, 1H).
8d	6.96–8.41 (m, aromatic protons).
8f	6.96–7.57 (m, 11H), 7.81 (d, 1H), 8.09 (d, 2H), 8.22 (d, 1H) and 8.38 (t, 1H).
13a	1.28 (d, 6H), 2.66 (s, 3H), 2.97–2.97 (sep., 1H), 7.26–7.30 (d, 2H), 7.64–7.68 (d, 2H), 7.90 (s, 1H) and 10.7 (s, br., 1H).
13b	1.27 (d, 6H), 2.90–2.99 (sept., 1H), 4.47 (s, 2H), 7.26–7.72 (m, 9H), 8.10 (s, 1H) and 13.26 (s, br., 1H).
14a	2.7 (s, 3H), 6.11 (s, 2H), 6.99–7.26 (m, 3H), 8.16 (s, 1H) and 13.25 (s, br., 1H).
14b	4.46 (s, 2H), 6.12 (s, 2H), 7.26–7.85 (m, 8H), 8.17 (s, 1H) and 13.26 (s, br. 1H).
18a	1.25 (d, 6H), 1.40 (t, 3H), 2.90–2.97 (sept., 1H), 4.45 (q, 2H), 7.25–7.71 (m, 5H), 7.91 (d, 2H), 7.97 (d, 2H) and 8.38 (s, 1H).
18f	1.25 (d, 6H), 2.94 (sep., 1H), 7.22–8.12 (m, 12H) and 8.41 (s, 1H).
19a	1.43 (t, 3H), 4.45 (q, 2H), 6.02 (s, 2H), 6.86-8.00 (m, 8H) and 8.30 (s, 1H).
19f	6.02 (s, 2H), 6.80–8.40 (m, 12H).
24a	7.11–7.51 (m, 15H), 7.96–8.00 (d, 2H) and 8.19 (t, 1H).
24b	1.28 (d, 6H), 2.94 (sep., 1H), 7.22–8.12 (m, 14H) and 8.31 (s, 1H).
24c	6.01 (s, 2H), 7.22–8.12 (m, 13H) and 8.35 (s, 1H).

Microanalytical Center of the University of Cairo, Giza, Egypt. Hydrazonoyl halides **4a–h** and **23** were prepared according to the literature.[7–14]

Synthesis of Alkyl Carbodithioates 3a,b, and (13–17)a,b

An appropriate cinnamaldehyde, cumenaldehyde, piperenal, pyrrole-2-carboxaldehyde, 3-formylindole, or 2,4-dihydroxybenzaldehyde (0.01 mol) was added to solution of the appropriate alkyl hydrazinecarboditioates[15,16] (0.01 mol) in 2-propanol (50 ml) while stirring at room temperature. The reaction mixture was stirred for 2 h. The solid so formed was collected and crystallized from ethanol to give **3a**,**b** and (**13–17**)**a**,**b**, yields (87–83%) respectively (cf. Tables I and II).

Synthesis of 2,3-Dihydro-1,3,4-thiadiazole Derivatives 8a–g, (18–22)a–h, and 24a–e

Method A

A mixture of the appropriate alkyl carbodithioates **3a**,**b** or (**13–17**)**a**,**b** (0.005 mol) and the appropriate hydrazonoyl halides **4a–h** or **23** and triethylamine (0.75 ml, 0.005 mol) in ethanol (20 ml) was stirred for 30 min. The resulting product was collected and crystallized from the proper solvent to give 2,3-dihydro-1,3,4-thiadiazoles (**8**, **18–22**)**a–h** and **24a–e**, respectively, in good yield (cf. Tables I and II).

Method B

A mixture of 5-hydrazono-4-phenyl-4,5-dihydro-1,3,4-thiadiazole-2-carboxylic acid ethyl ester (**9**) (1.3 g, 0.005 mol) and the appropriate of aldehydes (cinnamaldehyde, piperenal, cumenaldehyde, pyrrole-2-carboxaldehyde, 3-formylindole, or 2,4-dihydroxybenzaldehyde) (0.005 mmol) in ethanol (30 ml) was stirred for 2 h. The solid was collected and crystallized from the proper solvent to give in all respects (m.p., nixed m.p., and spectra) with the corresponding prepared in method A.

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