Table I. List of the Newly Synthesized Compounds

compd (color)^a	mp, °C	yield, %	cryst solv^b	IR, cm^{-1}	^{1}H NMR, ppm
IVa (yellow)	>280	80	b	3400–3200 (NH_2 and NH); 2200 (CN); 1650 (C=N)	
IVb (yellow)	>280	82	b	3400–3200 (NH_2 and NH); 2200 (CN); 1640 (C=N)	3.2 (m, br, 2 H, 2 CH); 3.6 (br, 2 H, NH_2); 6.8–8.6 (m, 10 H, pyridyl and phenyl protons)
V (yellow)	>280	75	c	3400, 3250 (NH_2 and NH); 1680 (conjugated ester CO); 1640 (C=N)	1.3 (t, 3 H, CH_3); 2.4 (s, 3 H, CH_3); 3.6 (br, 2 H, NH_2); 4.2 (q, 2 H, CH_2); 5.85 (s, 1 H, methine CH); 7.4–8.6 (m, 6 H, pyridyl and NH protons)
VI (yellow)	>280	78	d	3450, 3250 (NH_2 and NH); 1690 (ring CO); 1640 (C=N)	2.3 (s, 3 H, CH_3); 4.0 (br, 2 H, NH_2); 6.9–8.6 (m, 7 H, aromatic and NH protons)
VIIIa (buff)	>280	92	b	3400–3200 (NH_2); 2200 (CN); 1650 (C=N); 1610 (C=C)	
VIIIb (brown)	235	90	b	3400, 3300–3100 (NH_2); 1680 (ester CO); 1620 (C=C)	1.3 (t, 3 H, CH_3); 3.8 (br, 2 H, NH_2); 4.2 (q, 2 H, CH_2); 7.4–8.2 (m, 5 H, pyridyl protons); 8.4 (br, 2 H, NH_2)
VIIIc (brown)	>280	88	b	3450–3200 (NH_2); 2200 (CN); 1640 (C=N)	6.8–8.2 (m, 10 H, pyridyl and phenyl protons); 8.5 (br, 2 H, NH_2)

^{a} Satisfactory elemental analyses were found. ^{b} Ethanol. ^{c} DMF. ^{d} Acetic acid.

the appropriate amount of IIa,b in ethanol (50 mL) was refluxed with piperidine (1 mL) until the reaction was complete (TLC control) (time ranges from 2 to 4 h). The solvent was triturated with a little water and then acidified with concentrated hydrochloric acid. The resulting solid products were collected by filtration and crystallized from the proper solvent (cf. Table I).

Ethyl β-[5-Amino-4-(3-pyridylazo)pyrazol-3-yl]aminocrotonate (V). A mixture of Ia (0.01 mol) and ethyl acetoacetate (1.0 mL) in ethanol (50 mL) were heated on a boiling water bath for 2 h. The solvent was then evaporated in vacuo and the remaining product poured onto water. The solid product, formed on standing, was collected by filtration and crystallized from the proper solvent (cf. Table I).

Cyclization of V. A solution of V (2 g) in acetic acid (50 mL) was heated under reflux for 3 h. The solvent was then evaporated in vacuo then triturated with water. The solid product, so formed, was collected by filtration and crystallized from the proper solvent (cf. Table I).

Reaction of Diazotized Ia with Active Hydrogen Compounds. A solution of 0.01 mol of diazotized Ia (prepared following the procedure described by Elnagdi et al. (*7*)) was added to a solution of an appropriate active hydrogen compound in ethanol. (The diazonium salts should be used directly. Gradual decomposition in solution takes place on standing. *Caution*: Care should be taken in attempting isolation of diazonium salts or the diazo compounds in the solid state as some of these diazo compounds explode readily.) The solid product was collected by filtration and crystallized from the proper solvent (cf. Table I).

Registry No. Ia, 97732-47-3; IIa, 2700-22-3; IIb, 2025-40-3; IVa, 97732-48-4; IVb, 97732-49-5; V, 97732-50-8; VI, 97732-51-9; VII, 97732-52-0; VIIIa, 97732-53-1; VIIIb, 97732-54-2; VIIIc, 97732-55-3; $CH_2(CN)_2$, 109-77-3; $EtOC(O)CH_2CN$, 105-56-6; $PhC(O)CH_2CN$, 614-16-4.

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Synthesis of Some 3-(Arylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidines

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The synthesis of 3-(arylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidines has been described by the oxidative debenzylation of the corresponding 1-(ethylethylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets. These compounds have been characterized by the direct oxidation of the corresponding 2,4-dithiobiurets and also by IR spectra.

Our earlier work (*1*, *2*) on the synthesis of 3-(arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines led us to prepare 3-(arylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidines as new analogues for evaluation of the biological activity of this class of compounds. It was of interest to assess the effect of alkyl substituted thiosemicarbazone moiety in the resulting dithiazolidene derivatives.

Experimental Section

S-Benzylisoethyl methyl ketone thiosemicarbazone and the related 1-(ethylethylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets (Table I), 3-(arylimino)-5-(ethylethylidenehydrazido)-

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Table I. Synthesis of 1-(Ethylethylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets

5-aryl-	mp, °C	% yield	mol formula[b]
5-phenyl-[a]	180	60	$C_{19}H_{22}N_4S_2$
5-*o*-tolyl-	112	75	$C_{20}H_{24}N_4S_2$
5-*p*-tolyl-	132	72	$C_{20}H_{24}N_4S_2$
5-*o*-chlorophenyl-	164	65	$C_{19}H_{21}N_4S_2Cl$
5-*p*-chlorophenyl-	182	78	$C_{19}H_{21}N_4S_2Cl$
5-*o*-methoxyphenyl-	175	70	$C_{20}H_{24}N_4S_2O$
5-*p*-methoxyphenyl-	146	80	$C_{20}H_{24}N_4S_2O$
5-*p*-ethoxyphenyl-	177	75	$C_{21}H_{26}N_4S_2O$

[a] Typical IR frequencies (cm^{-1}) of 1-(ethylethylideneamino)-5-phenyl-2-*S*-benzyliso-4-thiobiuret: 3175 (m), NH stretching, 1595 (m) N–C=N grouping, 1125 (m), 1145 (vs), 1195 (w), N–C(=S)–N grouping, 1625 (s), C=N stretching. [b] All of these compounds gave elemental analysis (C, H, N, S) within ±0.40% of the calculated values.

Table II. 3-(Arylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidines: Oxidative Debenzylation of 1-(Ethylethylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets with Liquid Bromine in Chloroform

3-arylimino	mp, °C	% yield	mol formula[b]
3-phenylimino-[a]	140	60	$C_{12}H_{14}N_4S_2$
3-*o*-tolylimino-	155	78	$C_{13}H_{16}N_4S_2$
3-*p*-tolylimino-	147	90	$C_{13}H_{16}N_4S_2$
3-*o*-chlorophenylimino-	175	70	$C_{12}H_{13}N_4S_2Cl$
3-*p*-chlorophenylimino-	130	85	$C_{12}H_{13}N_4S_2Cl$
3-*o*-methoxyphenylimino-	160	80	$C_{13}H_{16}N_4S_2O$
3-*p*-methoxyphenylimino-	154	75	$C_{13}H_{16}N_4S_2O$
3-*p*-ethoxyphenylimino-	144	78	$C_{14}H_{18}N_4S_2O$

[a] Typical IR frequencies (cm^{-1}) of 3-(phenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidines: C=N, 1625 (s), ring –S–S linkage 480 (s), 3175 (m), N–H stretching. [b] All of these compounds gave elemental analysis (C, H, N, S) within ±0.40% of the calculated values.

Table III. Synthesis of 1-(Ethylethylideneamino)-5-aryl-2,4-dithiobiurets by Reductive Debenzylation of 1-(Ethylethylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets with Hydrogen Sulfide in Pyridine–Triethylamine

2-*S*-benzyliso-4-thiobiurets reduced	2,4-dithiobiurets formed	mp, °C	% yield	mol[b] formula
1-(ethylethylideneamino)-5-phenyl-	1-(ethylethylideneamino)-5-phenyl-[a]	175	65	$C_{12}H_{16}N_4S_2$
1-(ethylethylideneamino)-5-*o*-tolyl-	1-(ethylethylideneamino)-5-*o*-tolyl-	123	65	$C_{13}H_{18}N_4S_2$
1-(ethylethylideneamino)-5-*p*-tolyl-	1-(ethylethylideneamino)-5-*p*-tolyl-	115	60	$C_{13}H_{18}N_4S_2$
1-(ethylethylideneamino)-5-(*o*-chlorophenyl)	1-(ethylethylideneamino)-5-(*o*-chlorophenyl)-	127	72	$C_{12}H_{15}N_4S_2Cl$
1-(ethylethylideneamino)-5-(*p*-chlorophenyl)	1-(ethylethylideneamino)-5-(*p*-chlorophenyl)-	134	80	$C_{12}H_{15}N_4S_2Cl$
1-(ethylethylideneamino)-5-(*o*-methoxyphenyl)-	1-(ethylethylideneamino)-5-(*o*-methoxyphenyl)-	141	78	$C_{13}H_{18}N_4S_2O$
1-(ethylethylideneamino)-5-(*p*-methoxyphenyl)-	1-(ethylethylideneamino)-5-(*p*-methoxyphenyl)-	108	85	$C_{13}H_{18}N_4S_2O$
1-(ethylethylideneamino)-5-(*p*-ethoxyphenyl)	1-(ethylethylideneamino)-5-(*p*-ethoxyphenyl)-	156	75	$C_{14}H_{20}N_4S_2O$

[a] Typical IR frequencies (cm^{-1}) of 1-(ethylethylideneamino)-5-phenyl-2,4-dithiobiuret: 3390 (w), NH stretching, 1155 (m), shows NC(=S)N grouping, 1625 (s), C=N grouping. [b] All of these compounds gave elemental analysis (C, H, N, S) within ±0.40% of the calculated values.

1,2,4-dithiazolidenes (Table II) and 1-(ethylethylideneamino)-5-aryl-2,4-dithiobiurets (Table III) were synthesized by the procedure reported earlier (*1*–*3*).

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Registry No. 1-(Ethylethylideneamino)-5-phenyl-2-*S*-benzyliso-4-thiobiuret, 97691-35-5; 1-(ethylethylideneamino)-5-(2-methylphenyl)-2-*S*-benzyliso-4-thiobiuret, 97691-36-6; 1-(ethylethylideneamino)-5-(4-methylphenyl)-2-*S*-benzyliso-4-thiobiuret, 97691-37-7; 1-(ethylethylideneamino)-5-(2-chlorophenyl)-2-*S*-benzyliso-4-thiobiuret, 97691-38-8; 1-(ethylethylideneamino)-5-(4-chlorophenyl)-2-*S*-benzyliso-4-thiobiuret, 97691-39-9; 1-(ethylethylideneamino)-5-(2-methoxyphenyl)-2-*S*-benzyliso-4-thiobiuret, 97703-37-2; 1-(ethylethylideneamino)-5-(4-methoxyphenyl)-2-*S*-benzyliso-4-thiobiuret, 97691-40-2; 1-(ethylethylideneamino)-5-(4-ethoxyphenyl)-2-*S*-benzyliso-4-thiobiuret, 97691-41-3; 3-(phenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidine, 97691-42-4; 3-(4-methylphenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidene, 97691-43-5; 3-(4-methylphenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidine, 97691-44-6; 3-(2-chlorophenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidine, 97691-45-7; 3-(4-chlorophenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidine, 97691-46-8; 3-(2-methoxyphenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidine, 97691-47-9; 3-(4-methoxyphenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidine, 97691-48-0; 3-(4-ethoxyphenylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidine, 97691-49-1; 1-(ethylethylideneamino)-5-phenyl-2,4-dithiobiuret, 97691-50-4; 1-(ethylethylideneamino)-5-(2-methylphenyl)-2,4-dithiobiuret, 97691-51-5; 1-(ethylethylideneamino)-5-(4-methylphenyl)-2,4-dithiobiuret, 97691-52-6; 1-(ethylethylideneamino)-5-(2-chlorophenyl)-2,4-dithiobiuret, 97691-53-7; 1-(ethylethylideneamino)-5-(4-chlorophenyl)-2,4-dithiobiuret, 97691-54-8; 1-(ethylethylideneamino)-5-(2-methoxyphenyl)-2,4-dithiobiuret, 97691-55-9; 1-(ethylethylideneamino)-5-(4-methoxyphenyl)-2,4-dithiobiuret, 97691-56-0; 1-(ethylethylideneamino)-5-(4-ethoxyphenyl)-2,4-dithiobiuret, 97691-57-1.

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