NEW COMPOUNDS

Some 3-(Arylimino)-5-(*N*-benzylidenehydrazono)-1,2,4-dithiazolidines. Oxidative Debenzylation and Cyclization of 5-Aryl-1-(benzylideneamino)-2-*S*-benzyliso-2,4-dithiobiurets

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Synthesis of 3-(arylimino)-5-(*N*-benzylidenehydrazono)-1,2,4-dithiazolidines (IVa–e) has been achieved by the oxidative debenzylation and cyclization of the corresponding 5-aryl-1-(benzylideneamino)-2-*S*-benzyliso-2,4-dithiobiurets (IIa–e). These dithiazolidines have been characterized by their preparation from the corresponding 2,4-dithiobiurets (IIIa–e) and also by IR spectra.

Our interest in the chemistry of 3-arylimino-5-(*N*-substituted hydrazono)-1,2,4-dithiazolidines (*1*, *2*) and in the study of oxidative debenzylation and cyclization reaction has led us to extend the reaction to a new series of isodithiobiurets leading to the synthesis of some entirely new 3-arylimino-5-(*N*-benzylidenehydrazono)-1,2,4-dithiazolidines.

The present communication describes the synthesis of certain 5-aryl-1-(benzylideneamino)-2-*S*-benzyliso-2,4-dithiobiurets (IIa–e) and their facile conversion to the related 3-arylimino-5-(*N*-benzylidenehydrazono)-1,2,4-dithiazolidines (IVa–e). (See Scheme I.)

Experimental Section

Melting points were recorded on a Kofler hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-720). The proton NMR spectra were recorded on a Varian A-60D spectrometer using Me_4Si as internal standard.

Benzaldehyde thiosemicarbazone was prepared according to the known procedure (*3*) and its benzylation was performed with benzyl chloride in the presence of sodium ethoxide (*4*).

5-Aryl-1-(benzylideneamino)-2-S-benzyliso-2,4-dithiobiurets (IIa–e). The details of a typical experiment are as follows: To a dry benzene extract of *S*-benzylisobenzaldehyde thiosemicarbazone (2.5 g; 0.009 mol) was added benzyl isothiocyanate (1.39 g; 0.009 mol) and the mixture was refluxed for 2 h. The excess of solvent was evaporated and the semisolid mass thus obtained on washing with petroleum ether followed by addition of a little ethanol gave a crystalline product. It was recrystallized from ethanol, mp 122 °C (yield 76%) (Table I).

3-Arylimino-5-(N-benzylidenehydrazono)-1,2,4-dithiazolidines (IVa–e). Method A. Oxidative Debenzylation of IIa–e. The substituted 2-*S*-benzyliso-2,4-dithiobiuret made into paste with a little chloroform was treated with liquid bromine until the color of the bromine persisted. The reaction mixture warmed up considerably evolving lachrymatory fumes of benzyl bromide. It was allowed to stand over 1 h and washed with ether. On treatment with ethanol the hydrobromide of the related 1,2,4-dithiazolidine separated out as a crystalline mass. Treatment of these with ammonia afforded the free bases (IVa–e) which were crystallized from ethanol. The dithiazolidine bases so obtained showed no depression in melting point when

Scheme I

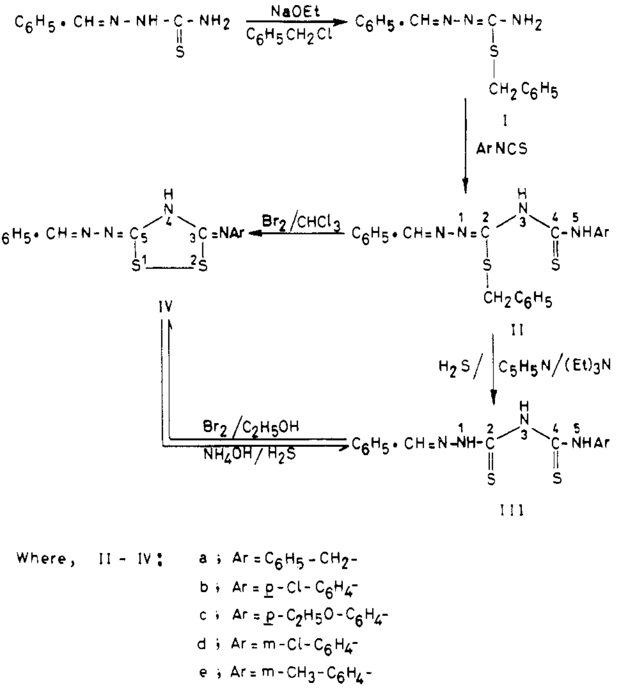

Table I. Characterization Data of Compounds IIa–e[a]

compd	mp, °C	yield, %	molecular formula
IIa	122	76	$C_{23}H_{22}N_4S_2$
IIb	140	84	$C_{22}H_{19}ClN_4S_2$
IIc	134	69	$C_{24}H_{24}N_4OS_2$
IId	139	81	$C_{22}H_{19}ClN_4S_2$
IIe	120	71	$C_{23}H_{22}N_4S_2$

[a] Typical IR frequencies (cm^{-1}) of 5-benzyl-1-(benzylideneamino)-2-*S*-benzyliso-2,4-dithiobiuret: 3390 m (N–H stretching) (*5a*, *6*), 1125, 1148 s, 1200 w (NC(=S)N grouping) (*5a*), 1595 w (N–C=N– grouping) (*5b*). The proton NMR of 5-benzyl-1-(benzylideneamino)-2-*S*-benzyliso-2,4-dithiobiuret: ($CDCl_3$) δ 7.3 (s, 15 H arom; 2 H, 2NH), 8.0 (s, 1 H, CH), 4.7–4.8 (m (doublet), 2 H, N-CH_2), 4.15 (s, 2 H, S-CH_2). Carbon and hydrogen analyses were in satisfactory agreement with the calculated values (C, ±0.34; H, ±0.25).

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Table II. Characterization Data of Compounds IVa-e[a]

compd	mp, °C	yield, %	molecular formula
IVa	156	85	$C_{16}H_{14}N_4S_2$
IVb	240	81	$C_{15}H_{11}ClN_4S_2$
IVc	224	77	$C_{17}H_{16}N_4OS_2$
IVd	168	63	$C_{15}H_{11}ClN_4S_2$
IVe	216	69	$C_{16}H_{14}N_4S_2$

[a] Typical IR frequencies (cm^{-1}) of 3-benzylimino-5-(*N*-benzylidenehydrazono)-1,2,4-dithiazolidine: 3200 m (N–H stretching), 1628 s (C=N) (*5*), 495 s, (ring –S–S– linkage) (*7*). The proton NMR of 3-benzylimino-5-(*N*-benzylidenehydrazono)-1,2,4-dithiazolidine: ($CDCl_3$) δ 7.3 (s, 10 H, arom; 1 H, NH), 7.9 (s, 1 H, CH), 4.5 (m, 2 H, CH_2). Carbon and hydrogen analyses were in satisfactory agreement with the calculated values (C, ±0.34; H, ±0.25).

Table III. Characterization Data of Compounds IIIa-e[a]

compd	mp, °C	yield, %	molecular formula
IIIa	140	60	$C_{16}H_{16}N_4S_2$
IIIb	169	59	$C_{15}H_{13}ClN_4S_2$
IIIc	181	63	$C_{17}H_{18}N_4OS_2$
IIId	110	49	$C_{15}H_{13}ClN_4S_2$
IIIe	108	48	$C_{16}H_{16}N_4S_2$

[a] Typical IR frequencies (cm^{-1}) of 5-benzyl-1-(benzylideneamino)-2,4-dithiobiuret: 3398 w (N–H stretching) (*6*), 1156 m (shows NC(=S)N grouping) (*5a*), 1625 s (C=N grouping) (*5*). The proton NMR of 5-benzyl-1-(benzylideneamino)-2,4-dithiobiuret: ($CDCl_3$) δ 7.2 (s, 10 H, arom; 3 H, 3NH), 7.9 (s, 1 H, CH), 4.6-4.7 (m, (doublet), 2 H, N-CH_2). Carbon and hydrogen analyses were in satisfactory agreement with the calculated values (C, ±0.34; H, ±0.25).

mixed with the authentic samples obtained by the oxidation of the corresponding 1,5-disubstituted 2,4-dithiobiurets (Table II).

Method B. Oxidation of IIIa-e. 5-Aryl-1-(benzylideneamino)-2,4-dithiobiurets (Table III) were oxidized with bromine in dilute ethanol and on addition of excess of ether the hydrobromide of the corresponding 3-arylimino-5-(*N*-benzylidenehydrazono)-1,2,4-dithiazolidines precipitated. These on basification with ammonia afforded the free bases (IVa-e) which were crystallized from ethanol (Table II).

5-Aryl-1-(benzylideneamino)-2,4-dithiobiurets (IIIa-e). Method A. Reductive Debenzylation of IIa-e. 5-Aryl-1-(benzylideneamino)-2-*S*-benzyliso-2,4-dithiobiurets were dissolved in pyridine–triethylamine solution (1:6) and a stream of dry H_2S was passed for 4 h. The resulting reaction mixture after filtration was poured over crushed ice and acidified with dilute hydrochloric acid when the expected dithiobiurets (IIIa–e) precipitated. These were filtered and crystallized from ethanol (Table III).

Method B. Reduction of IV. The dithiazolidines (IVa–e) were dissolved in hot ethanolic ammoniacal hydrogen sulfide solution and a stream of hydrogen sulfide passed for 4 h. The clear solution on dilution with water or acidification afforded the related dithiobiurets. These were crystallized from ethanol (Table III).

The characterization of each compound was done by observing undepressed mixed melting points with the authentic samples obtained by conventional reduction of the isodithiobiurets (Table III) and also by identical IR spectra.

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Registry No. I, 7441-56-7; IIa, 83710-17-2; IIb, 83710-18-3; IIc, 83710-19-4; IId, 83710-20-7; IIe, 83710-21-8; IIIa, 83710-22-9; IIIb, 83710-23-0; IIIc, 83710-24-1; IIId, 83710-25-2; IIIe, 83710-26-3; IVa, 83710-27-4; IVb, 83710-28-5; IVc, 83710-29-6; IVd, 83710-30-9; IVe, 83710-31-0; benzaldehyde thiosemicarbazone, 1627-73-2.

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