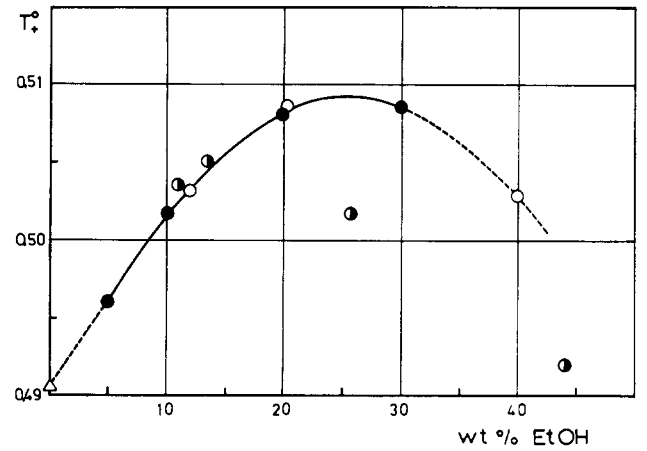

Figure 1. Variation of the limiting cation transference numbers with wt % of ethanol: (●) present work; (○) ref *2*; (◑) ref *3*; (△) ref (*7*).

is a greater amount of water in the cosphere of the ion with respect to the bulk solvent, the microscopic viscosity around the ion falls and the mobility of the ion increases (ascending line in Figure 1). On the contrary, a greater amount of ethanol in the cosphere of the ion with respect to the bulk solvent should increase the viscosity around the ion, and, therefore, its mobility should diminish (descending line in Figure 1).

From the T_+^0 values in the present work (by using eq 2) and the limiting equivalent conductances, Λ^0, known previously (*4*), limiting ionic conductances have been determined (Table II).

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NEW COMPOUNDS

3-(Arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines: Oxidative Debenzylation and Cyclization of 1-(Phenylbenzylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets

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A number of 3-(arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines have been synthesized by the oxidative debenzylation and cyclization of the corresponding 1-(phenylbenzylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets. The characterization of these compounds has been achieved by the direct oxidation of the corresponding 2,4-dithiobiurets and also by IR spectra.

Oxidation of 2,4-dithiobiurets to the related 1,2,4-dithiazolidines has been a well-known method (*1–6*) of synthesis. Recently, it has been reported that substituted 1,2,4-dithiazolidines could also be synthesized by the oxidative dealkylation of the related isodithiobiurets (*7–12*). In light of these observations, it was thought of interest to extend the oxidative debenzylation and cyclization reaction to the synthesis of certain hitherto unreported 3-(arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines.

This paper describes the synthesis of certain new 3-(arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines by the oxidative debenzylation and ring closure of the related 1-(phenylbenzylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets. The reaction can be represented as shown in Scheme I.

Experimental Section

Melting points were determined by a Kofler hot stage apparatus and are uncorrected.

Benzophenone thiosemicarbazone (I) was prepared by the known procedure (*13*) and its *S*-benzyl derivative (II) was obtained by benzylation with benzyl chloride in the presence of sodium ethoxide (*14*).

1-(Phenylbenzylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets (III). The details of a typical experiment are as follows: Benzene solution of *S*-benzylisobenzophenone thiosemicarbazone (3.43 g) was refluxed with phenyl isothiocyanate (1.35 g) for 1 h. On evaporation of the solvent, 1-(phenylbenzylideneamino)-5-phenyl-2-*S*-benzyliso-4-thiobiuret was obtained as a semisolid, which on washing with petroleum ether and on addition of a little ethanol became granular; mp 98 °C (yield 3.5 g, 75%). The results of these experiments are summarized in Table I.

3-(Arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines (V). (I) Oxidative Debenzylation of 1-(Phenylbenzylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets. The

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

5-aryl	mp, °C	% yield	molecular formula[b]
5-phenyl-[a]	98	75	$C_{28}H_{24}N_4S_2$
5-*o*-tolyl-	114	72	$C_{29}H_{26}N_4S_2$
5-*p*-tolyl-	110	60	$C_{29}H_{26}N_4S_2$
5-*o*-chlorophenyl-	116	62	$C_{28}H_{23}N_4S_2Cl$
5-*p*-chlorophenyl-	94	68	$C_{28}H_{23}N_4S_2Cl$
5-*o*-methoxyphenyl-	35	60	$C_{29}H_{26}N_4S_2O$
5-*p*-methoxyphenyl-	42	60	$C_{29}H_{26}N_4S_2O$
5-*p*-ethoxyphenyl-	92	78	$C_{30}H_{28}N_4S_2O$

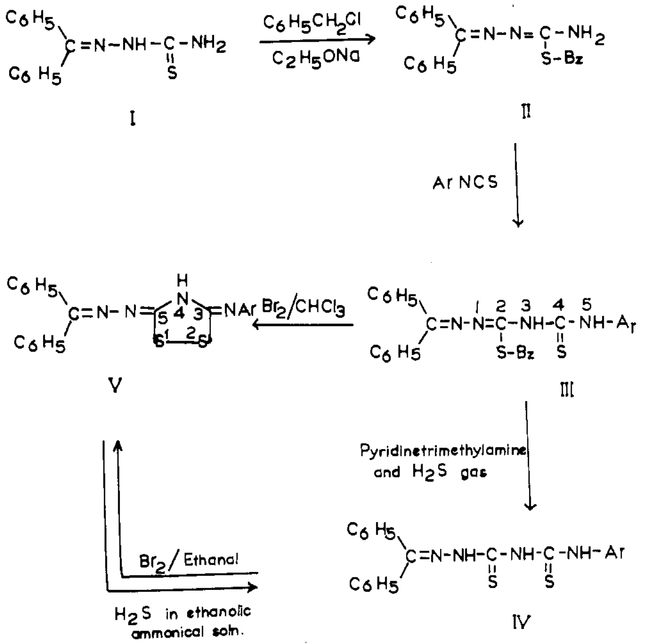
[a] Typical IR frequencies (cm^{-1}) of 1-(phenylbenzylideneamino)-5-phenyl-2-*S*-benzyliso-4-thiobiuret: 3200 (m), N–H stretching; 1120 (m), 1145 (vs), 1200 (w), NC(=S)N grouping; 1590 (w), N–C=N– grouping; 1620 (s), C=N stretching. [b] All of these compounds gave elemental analysis (C, H, N, S) within ±0.40% of the calculated values.

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

3-arylimino-	mp, °C	% yield	molecular formula[b]
3-phenylimino-[a]	142	70	$C_{21}H_{16}N_4S_2$
3-*o*-tolylimino-	156	78	$C_{22}H_{18}N_4S_2$
3-*p*-tolylimino-	164	85	$C_{22}H_{18}N_4S_2$
3-*o*-chlorophenylimino-	202	65	$C_{21}H_{15}N_4S_2Cl$
3-*p*-chlorophenylimino-	154	80	$C_{21}H_{15}N_4S_2Cl$
3-*o*-methoxyphenylimino-	160	68	$C_{22}H_{18}N_4S_2O$
3-*p*-methoxyphenylimino-	148	72	$C_{22}H_{18}N_4S_2O$
3-*p*-ethoxyphenylimino-	190	75	$C_{23}H_{20}N_4S_2O$

[a] Typical IR frequencies (cm^{-1}) of 3-(phenylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidine: C=N, 1620 (s); ring –S–S– linkage 480 (s); 3200 (m), N–H stretching. [b] All of these compounds gave elemental analysis (C, H, N, S) within ±0.40% of the calculated values.

Scheme I[a]



[a] Where Ar = phenyl-, *o*-tolyl-, *p*-tolyl-, *o*-chlorophenyl-, *p*-chlorophenyl-, *o*-methoxyphenyl-, *p*-methoxyphenyl-, or *p*-ethoxyphenyl-.

substituted 2-*S*-benzyliso-4-thiobiuret made into paste with a little chloroform or carbon tetrachloride was treated with liquid bromine until the color of bromine persisted. The reaction mixture warmed up considerably evolving lachrymatory fumes of benzyl bromide. After 30 min, the semisolid product was washed first with ether and then with a mixture of ether and a small amount of ethanol, when the hydrobromide of the oxidation product separated out as a crystalline mass. On treatment with ammonia the free base was obtained, which was thoroughly washed with ether and crystallized from ethanol. The dithiazolidine bases thus obtained showed no depression in melting point when mixed with the authentic samples obtained by the oxidation of the corresponding 1,5-disubstituted-2,4-dithiobiurets. The results are presented in Table II.

(II) Oxidation of 1-(Phenylbenzylideneamino)-5-aryl-2,4-dithiobiurets (IV) with Bromine in Dilute Ethanol. The 2,4-dithiobiurets listed in Table III were oxidized with bromine in ethanolic solution, and ether was added whereupon the hydrobromides of the respective dithiazolidines precipitated. The free bases were obtained by treating these products with ammonia. The bases were crystallized from ethanol or chlorobenzene (Table II).

1-(Phenylbenzylideneamino)-5-aryl-2,4-dithiobiurets (IV). (I) Reductive Debenzylation of 1-(Phenylbenzylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets (III). The desired isodithiobiuret (III) was dissolved in pyridine–triethylamine (6:1) solution, and a stream of dry hydrogen sulfide gas was passed through the solution for 3 h. The resulting solution on filtration, cooling, and neutralization with dilute hydrochloric acid afforded

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

2-*S*-benzyliso-4-thiobiurets reduced	2,4-dithiobiurets formed	mp, °C	% yield	molecular formula[b]
1-(phenylbenzylideneamino)-5-phenyl-	1-(phenylbenzylideneamino)-5-phenyl-[a]	146	60	$C_{21}H_{18}N_4S_2$
1-(phenylbenzylideneamino)-5-*o*-tolyl	1-(phenylbenzylideneamino)-5-*o*-tolyl-	124	68	$C_{22}H_{20}N_4S_2$
1-(phenylbenzylideneamino)-5-*p*-tolyl	1-(phenylbenzylideneamino)-5-*p*-tolyl-	115	70	$C_{22}H_{20}N_4S_2$
1-(phenylbenzylideneamino)-5-(*o*-chlorophenyl)-	1-(phenylbenzylideneamino)-5-(*o*-chlorophenyl)-	131	72	$C_{21}H_{17}N_4S_2Cl$
1-(phenylbenzylideneamino)-5-(*p*-chlorophenyl)-	1-(phenylbenzylideneamino)-5-(*p*-chlorophenyl)-	142	80	$C_{21}H_{17}N_4S_2Cl$
1-(phenylbenzylideneamino)-5-(*o*-methoxyphenyl)-	1-(phenylbenzylideneamino)-5-(*o*-methoxyphenyl)-	154	82	$C_{22}H_{20}N_4S_2O$
1-(phenylbenzylideneamino)-5-(*p*-methoxyphenyl)-	1-(phenylbenzylideneamino)-5-(*p*-methoxyphenyl)-	135	75	$C_{22}H_{20}N_4S_2O$
1-(phenylbenzylideneamino)-5-(*p*-ethoxyphenyl)-	1-(phenylbenzylideneamino)-5-(*p*-ethoxyphenyl)-	142	65	$C_{23}H_{22}N_4S_2O$

[a] Typical IR frequencies (cm^{-1}) of 1-(phenylbenzylideneamino)-5-phenyl-2,4-dithiobiuret: 3315 (w), N–H stretching; 1150 (m), shows NC(=S)N grouping; 1620 (s), C=N grouping. [b] All of these compounds gave elemental analysis (C, H, N, S) within ±0.40% of the calculated values. .

the expected dithiobiuret (IV). These were crystallized from ethanol. The results of these experiments are tabulated in Table III.

(II) Reduction of 3-(Arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines (V) by Ethanolic Ammoniacal Hydrogen Sulfide. The dithiazolidines were dissolved in hot ethanolic ammoniacal hydrogen sulfide solution, and a stream of hydrogen sulfide was passed through the solution for 3 h. The clear solution on dilution with water or acidification afforded the related dithiobiurets. These were crystallized from ethanol (Table III).

The identity of each product was established by mixture melting point technique with the authentic sample obtained by conventional reduction of the isodithiobiurets described in Table III and by identical IR spectra.

Acknowledgment

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Synthesis of Some Bromine-Containing 2,4-Diaminotriazines

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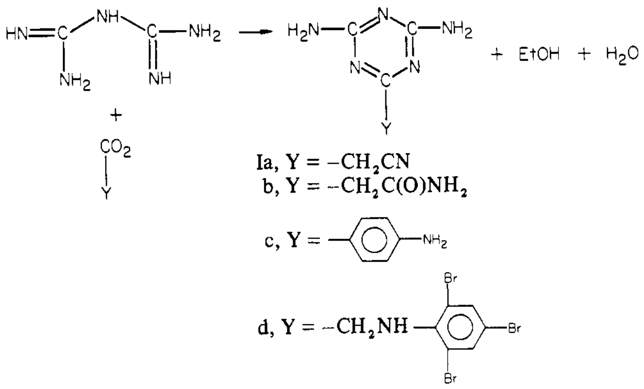
2,4-Diamino-1,3,5-triazines substituted in the 6-position with cyanomethyl (Ia), carbamoylmethyl (Ib), and 4-aminophenyl (Ic) groups were prepared by the reaction of the appropriate esters with biguanide and brominated in aqueous media to the dibromides IIa–c. The triazine Id, substituted in the 6-position with a 2,4,6-tribromoanilinomethyl group, was prepared by the reaction of biguanide with ethyl *N*-(2,4,6-tribromophenyl)glycinate (IV). The latter was prepared by the bromination of ethyl *N*-phenylglycinate in a mixture of water and acetic acid. *N*-(2,4,6-Tribromophenyl)glycinamide (V) was prepared by the reaction of IV with alcoholic ammonia. 2,4-Bis[bis(hydroxymethyl)amino]-6-(3,5-dibromo-4′-aminophenyl)-1,3,5-triazine (III) and 2,4-bis[bis(hydroxymethyl)amino]-6-(2′,4′,6′-tribromoanilinomethyl)-1,3,5-triazine (VI) were prepared by the reaction of IIc and Id, respectively, with aqueous formaldehyde. Some infrared data on the compounds are presented.

While investigating flame retardants for cotton textiles, I prepared some new 2,4-diaminotriazines with groups containing bromine.

Chance and Timpa reported an example of a brominated diaminotriazine (*1*). They prepared 2,4-diamino-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine (DABPT) by the reaction of ethyl γ-tribromobutyrate with biguanide. Ostrogovich reported an analogue of DABPT, 2,4-diamino-6-tribromomethyl-1,3,5-triazine, prepared by direct bromination of 2,4-diamino-6-methyl-1,3,5-triazine (*4*).

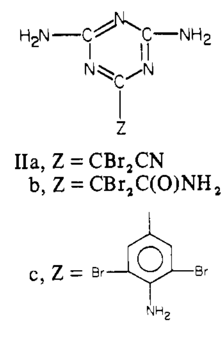
In this investigation compounds Ia–d were prepared by the reaction of biguanide with the appropriate ester YCO$_2$Et, as described by Thurston for compounds Ia (*7a*) and Ic (*7b*).



Ia, Y = $-CH_2CN$
b, Y = $-CH_2C(O)NH_2$
c, Y =
d, Y = $-CH_2NH-$

The ester required for Id, ethyl *N*-(2,4,6-tribromophenyl)glycinate (IV), was prepared by the reaction of ethyl *N*-phenylglycinate with bromine in a mixture of water and acetic acid. IV reacted with ammonia in ethanol solution to form *N*-(2,4,6-tribromophenyl)glycinamide (V). IV hydrolyzed readily in hydrochloric acid to the corresponding acid *N*-(2,4,6-tribromophenyl)glycine, a compound reported in the literature (*5*).

Compounds Ia–c were then allowed to react with bromine in aqueous media to form diaminotriazines IIa–c.



IIa, Z = CBr_2CN
b, Z = $CBr_2C(O)NH_2$
c, Z =

Crystalline methylol derivatives of IIc and Id, III and VI, respectively, were prepared by reaction with aqueous form-