Table VI. Root Mean Square (rms) Deviations for Different Ternary Systems with Use of Equation 2 at Different Temperatures

	rms^a				
	30 °C	40 °C	50 °C	60 °C	mean
toluene (1)–bromobenzene (2)–1-octanol (3)	0.0845	0.0787	0.0796	0.0911	0.0835
toluene (1)–1-hexanol (2)–1-octanol (3)	0.0606	0.0423	0.0351	0.0449	0.0457
bromobenzene (1)–1-hexanol (2)–1-octanol (3)	0.0465	0.0434	0.0499	0.0547	0.0485

^{a}rms deviation = $[\sum di^2/n]^{1/2}$ where n is the number of observations and $d = [(\eta_{\text{exptl}} - \eta_{\text{calcd}})/\eta_{\text{exptl}}]$.

sponding binary η_m–X–T data (*11*). A^*_{ijk} of eq 2 is the additional ternary constant to be evaluated by experimental ternary η_m–X–T data by the least-squares method. Such values of A_{ij}, B_{ij}, C_{ij}, and A^*_{ijk} are listed in Table V. The parameters included in Table IV were used as input in eq 2 for calculating η–X–T data showing root mean square deviations as listed in Table VI.

Acknowledgment

We are grateful to the authorities of the Jalpaiguri Government Engineering College, Jalpaiguri, India, for providing laboratory facilities.

Glossary

T	temperature, K
t	temperature, °C
X	mole fraction

Greek Letters

η	absolute viscosity, cP
ρ	density, g mL^{-1}

Subscripts

i	component in a mixture
m	mixture
1,2,3	component number in a mixture

Superscript

E	excess quantity

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Received for review August 4, 1989. Accepted October 13, 1989.

NEW COMPOUNDS

Synthesis of 1-Aryl-2-hydrazino-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thiones and Related Thiosemicarbazides

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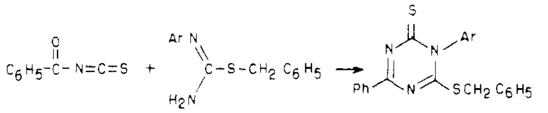
Different 1-aryl-2-(benzylthio)-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thiones have been synthesized by known methods. These triazines on treatment with hydrazine hydrate under suitable conditions afforded corresponding hydrazino derivatives. 1-Aryl-2-hydrazino-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione on interaction with aryl/alkyl isothiocyanates gave related thiosemicarbazides.

The presence of antituberculous (*1*, *2*), antibacterial, antiviral (*3*), and antifungal (*4*) activity in some substituted thiosemicarbazides prompted us to search for new members of this series containing the triazinyl moiety.

The present paper deals with the synthesis of 1-aryl-2-hydrazino-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thiones (II) and *N*-aryl/alkyl-*N*″-(1-aryl-4-phenyl-1,6-dihydro-6-thioxo-1,3,5-triazin-2-yl)thiosemicarbazides (III). The precursor 1-aryl-2-(benzylthio)-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (I) was obtained by condensation of benzoyl isothiocyanate (*5*) and

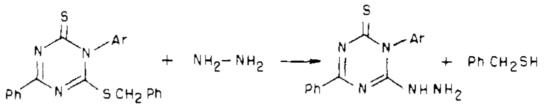
S-benzyl-*N*-arylisothiourea (*6*) as reported earlier (*7–11*). The hydrazinotriazines were obtained in good yields when equimolecular quantities of triazine (I) and hydrazine hydrate were stirred at 25 °C (room temperature) for a period of 6–8 h. The hydrazinotriazines (II) when reacted with isothiocyanates afforded related thiosemicarbazides (III).

(1)



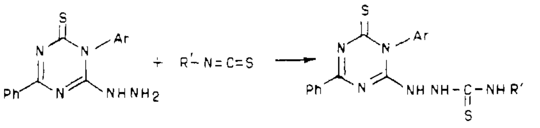
Ar = 2-ClC_6H_4(Ia), 4-ClC_6H_4 (Ib), 2-MeC_6H_4(Ic)

(2)



Ar = 2-ClC_6H_4(IIa), 4-ClC_6H_4 (IIb), 2-MeC_6H_4 (IIc)

(3)



Ar = 2-ClC_6H_4(IIIa), 4-ClC_6H_4 (IIIb), 2-MeC_6H_4 (IIIc)

Experimental Section

Melting points were obtained by using a Thomas Hoover stirred liquid apparatus and are uncorrected. NMR spectra, reported in parts per million (δ), were obtained with a JEOL FS 90Q Fourier transform spectrometer with Me_4Si as internal standard. IR spectra were obtained with a Perkin-Elmer 720 grating IR spectrometer. Elemental analyses for C, H, N, and S were within ±0.32% of the theoretical values, and they were submitted for review.

2-(Benzylthio)-1-(2-chlorophenyl)-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (Ia) (7–11). A solution of benzoyl isothiocyanate (6.5 g, 40 mmol) was gradually added with vigorous stirring to *S*-benzyl-*N*-(2-chlorophenyl)isothiourea (11.1 g, 40 mmol) in acetone (50 mL) over a period of 5 min. A golden yellow solid separated which was recrystallized from benzene: yield 9.5 g (56.3%); mp 214 °C; IR (Nujol) 1630 (C=N) 1090 (C=S), 670 (C-S-C) cm^{-1}; NMR ($CDCl_3$) δ 4.524 (s, 2 H, CH_2), 7.222–7.603 (m, 12 H, ArH), 8.524–8.619 (m, 2 H, ArH).

By a similar procedure, 2-(benzylthio)-1-(4-chlorophenyl)-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (Ib) was prepared: yield 10.0 g (59.31%); mp 215 °C; IR (Nujol) 1635 (C=N), 1100 (C=S), 675 (C-S-C) cm^{-1}; NMR ($CDCl_3$) δ 4.476 (s, 2 H, CH_2), 7.159–7.635 (m, 12 H, Ar*H*), 8.492–8.603 (m, 2 H, ArH).

2-(Benzylthio)-1-(2-methylphenyl)-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (Ic) was also prepared: yield 11.0 g (68.58%); mp 178 °C; IR (Nujol) 1625 (C=N), 1080 (C=S), 680 (C-S-C) cm^{-1}; NMR ($CDCl_3$) δ 2.190 (s, 3 H, CH_3), 4.476 (s, 2 H, CH_2), 7.048–7.55 (m, 12 H, ArH), 8.492–8.635 (m, 2 H, ArH).

1-(2-Chlorophenyl)-2-hydrazino-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (IIa) (12). 2-(Benzylthio)-1-(2-chlorophenyl)-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (8.4 g, 20 mmol) was dissolved in benzene (300 mL), hydrazine hydrate was added, and the reaction mixture was stirred for 8 h. A light brown product separated that was recrystallized from an ethanol/DMF (4:1) mixture: yield 4.2 g (63.7%); mp 160 °C; IR (Nujol) 3440, 3300, 3160 ($-NHNH_2$), 1640 (C=N), 1080 (C=S)) cm^{-1}.

By a similar procedure 1-(4-chlorophenyl)-2-hydrazino-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (IIb) was prepared: yield 4.0 g (60.70%); mp 172 °C; IR (Nujol) 3430, 3310, 3170 ($-NHNH_2$), 1645 (C=N), 1085 (C=S) cm^{-1}.

2-Hydrazino-1-(2-methylphenyl)-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (IIc) was also prepared: yield 3.8 g (61.49%); mp 145 °C; IR (Nujol) 3400, 3320, 3100 ($-NHNH_2$), 1630 (C=N), 1100 (C=S) cm^{-1}.

N-(2-Methylphenyl)-N″-[1-(2-chlorophenyl)-4-phenyl-1,6-dihydro-6-thioxo-1,3,5-triazin-2-yl] thiosemicarbazide (IIIc). 1-(2-Chlorophenyl)-2-hydrazino-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione (1.65 g, 5 mmol) was mixed with 2-methylphenyl isothiocyanate (0.89 g, 6 mmol), and the paste thus formed was heated in a water bath for a period of 45 min. The resulting product was washed with petroleum ether and recrystallized from ethanol: yield 1.80 g (75.2%), mp 226 °C; IR (Nujol) 3280, 3100 (-NH), 1520 ($N\text{-}C\!<^{N}_{S}$), 1640 (C=N), 1100 (C=S) cm^{-1}; NMR (DMSO-d_6) δ 3.717 (s, 3 H, CH_3), 7.000–8.443 (m, 13 H, ArH), 8.567–8.733 (d, 2 H, NH), 9.993 (s, 1 H, NH).

Similarly, other isothiocyanates were used, and the results are recorded in Table I. Compounds numbered 1–10 (Tables II and III) were prepared by condensing IIb and IIc with the appropriate isothiocyanates.

Table I. *N*-Aryl/alkyl-*N*″-[1-(2-chlorophenyl)-4-phenyl-1,6-dihydro-6-thioxo-1,3,5-triazin-2-yl]thiosemicarbazides (IIIa)[a]

no.	R	mp, °C	% yield
1	H	185	69
2	2-$CH_3C_6H_4$	226	58
3	3-$CH_3C_6H_4$	178	55
4	4-$CH_3C_6H_4$	217	64
5	2-$OCH_3C_6H_4$	214	56
6	3-$OMeC_6H_4$	189	67
7	4-$OCH_3C_6H_4$	181	59
8	2-ClC_6H_4	204	62
9	4-ClC_6H_4	197	70
10	Me	210	75

[a] All compounds were crystallized from ethanol.

Table II. *N*-Aryl/alkyl-*N*″-[1-(4-chlorophenyl)-4-phenyl-1,6-dihydro-6-thioxo-1,3,5-triazin-2-yl]thiosemicarbazides (IIIb)[a]

no.	R	mp, °C	% yield
1	C_6H_5	191	85
2	2-$CH_3C_6H_4$	207	70
3	3-$CH_3C_6H_4$	185	65
4	4-$CH_3C_6H_4$	228	72
5	2-$OCH_3C_6H_4$	181	58
6	3-$OCH_3C_6H_4$	196	63
7	4-$OCH_3C_6H_4$	190	68
8	2-ClC_6H_4	221	65
9	4-ClC_6H_4	235	70
10	Me	186	78

[a] All compounds were crystallized from ethanol.

Table III. *N*-Aryl/alkyl-*N*″-[1-(2-methylphenyl)-4-phenyl-1,6-dihydro-6-thioxo-1,3,5-triazin-2-yl]thiosemicarbazides (IIIc)[a]

no.	R	mp, °C	% yield
1	C_6H_5	179	80
2	2-$CH_3C_6H_4$	160	68
3	3-$CH_3C_6H_4$	175	64
4	4-$CH_3C_6H_4$	190	72
5	2-$OCH_3C_6H_4$	189	65
6	3-$OCH_3C_6H_4$	168	60
7	4-$OCH_3C_6H_4$	215	71
8	2-ClC_6H_4	178	70
9	4-ClC_6H_4	196	74
10	Me	208	78

[a] All compounds were crystallized from ethanol.

Acknowledgment

We are grateful to the Department of Chemistry, BHU, Varanasi, for providing the necessary facilities.

Registry No. Ia, 123100-05-0; Ib, 15998-34-2; Ic, 85442-31-5; IIa, 123100-06-1; IIb, 123100-07-2; IIc, 123100-08-3; IIIa (R = H), 123100-09-4; IIIa (R = *o*-MeC_6H_4), 123100-10-7; IIIa (R = *m*-MeC_6H_4), 123100-11-8; IIIa (R = *p*-MeC_6H_4), 123100-12-9; IIIa (R = *o*-$MeOC_6H_4$), 123100-13-0; IIIa (R = *m*-$MeOC_6H_4$), 123100-14-1; IIIa (R = *p*-$MeOC_6H_4$), 123100-15-2; IIIa (R = *o*-ClC_6H_4), 123100-16-3; IIIa (R = *p*-ClC_6H_4), 123100-17-4; IIIa (R = Me), 123100-18-5; IIIb (R = Ph), 123100-19-6; IIIb (R = *o*-MeC_6H_4), 123100-20-9; IIIb (R = *m*-MeC_6H_4), 123100-21-0; IIIb (R = *p*-MeC_6H_4), 123100-22-1; IIIb (R = *o*-$MeOC_6H_4$), 123123-96-6; IIIb (R = *m*-$MeOC_6H_4$), 123100-23-2; IIIb (R = *p*-$MeOC_6H_4$), 123100-24-3; IIIb (R = *o*-ClC_6H_4), 123100-25-4; IIIb (R = *p*-ClC_6H_4), 123100-26-5; IIIb (R = Me), 123100-27-6; IIIc (R = Ph), 123100-28-7; IIIc (R = *o*-MeC_6H_4), 123100-29-8; IIIc (R = *m*-MeC_6H_4), 123100-30-1; IIIc (R = *p*-MeC_6H_4), 123100-31-2; IIIc (R = *o*-$MeOC_6H_4$), 123100-32-3; IIIc (R = *m*-$MeOC_6H_4$), 123100-33-4; IIIc (R = *p*-$MeOC_6H_4$), 123100-34-5; IIIc (R = *o*-ClC_6H_4), 123100-35-6; IIIc (R = *p*-ClC_6H_4), 123123-97-7; IIIc (R = Me), 123100-36-7; PhCONCS, 532-55-8; HNCS, 463-56-9; *o*-MeC_6H_4NCS, 614-69-7; *m*-MeC_6H_4NCS, 621-30-7; *p*-MeC_6H_4NCS, 622-59-3; *o*-$MeOC_6H_4NCS$, 3288-04-8; *m*-$MeOC_6H_4NCS$, 3125-64-2; *p*-$MeOC_6H_4NCS$, 2284-20-0; *o*-ClC_6H_4NCS, 2740-81-0; *p*-ClC_6H_4NCS, 2131-55-7; MeNCS, 556-61-6; PhNCS, 103-72-0; *S*-benzyl-*N*-(2-chlorophenyl)isothiourea, 89070-01-9; *S*-benzyl-*N*-(4-chlorophenyl)isothiourea, 39536-26-0; *S*-benzyl-*N*-(2-methylphenyl)isothiourea, 123100-04-9.

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Received for review April 18, 1988. Revised November 4, 1988. Accepted June 21, 1989.