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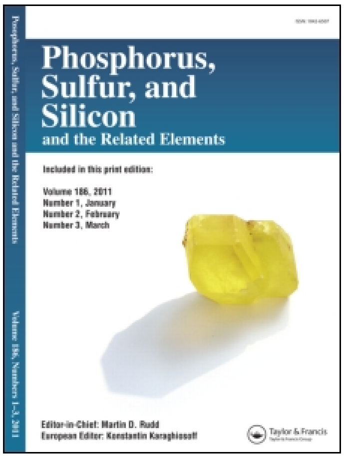

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SYNTHESIS AND REACTIONS OF SOME 4-ARYL-2-BENZYLMERCAPTO-1,6-DIHYDRO-6-THIONO-1,3,5-TRIAZINES

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Communication

SYNTHESIS AND REACTIONS OF SOME 4-ARYL-2-BENZYLMERCAPTO-1,6-DIHYDRO-6-THIONO-1,3,5-TRIAZINES

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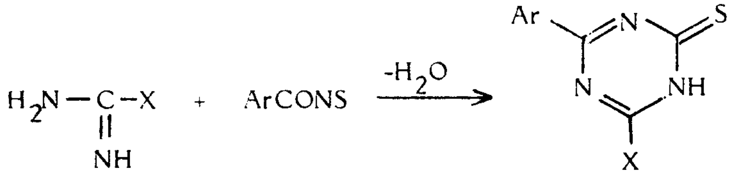
In the present work, we prepared some substituted 1,3,5-triazines (IVb, c) of expected biological activity and studied their reaction with some amines, namely, *p*-chloroaniline, isobutylamine and *m*-anisidine to give 2-substituted aminotriazines (Va–c), and also their reaction with methyl iodide to give (VIa–c).

It has been reported[1] that amidines, isoureas, isothioureas and guanidines **(Ia–d)** react with aroylisothiocyanates **(II)** to give 1,3,5-triazine thione derivatives **(IIIa–d)**. However, in some cases, formation of aroyl amidines predominate through an aroylation reaction which has been reported.[3,4] In the present investigation, S-benzylthiouronium chloride, a weak nucleophile, was chosen in order to ensure the mode[2] of addition of nucleophiles to $>C{=}S$ and/or $>C{=}O$ function of **(II)**.



(I) (II) (III)

a; X = Aryl or alkyl

b; X = OR

c; X = SR

d; X = NR_2

Also, it has been reported[2] that 2-*tert*-butylmercapto-4-phenyl-thiono-1,3,5-triazine reacts with diazomethane to give a mixture of S-methyl derivative and N-methyl derivative. However, treatment of the same compound with methyl iodide and sodium hydroxide gave only the *s*-methyl derivative.

TABLE I

Characterization data of **(IV)**, **(V)** and **(VI)**

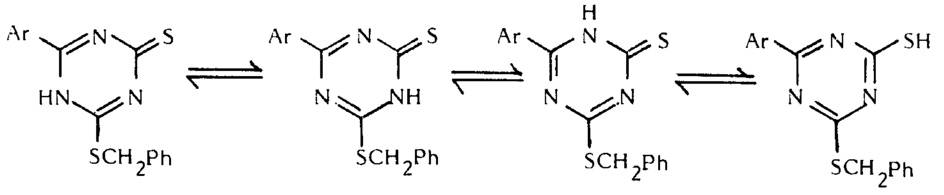
Compd. No.	Ar	R_1	R_2	M.p.°C Solvent*	Yield %	Mol. Formula	Found/Calcd. C	H	N	S	Cl%
IVb	*p*-CH_3–OC_6H_4	—	—	168–170	55	$C_{17}H_{15}N_3OS_2$	60.0	4.3	12.1	18.8	
				B			59.9	4.4	12.3	18.6	
IVc	*p*-CH_3–C_6H_4	—	—	169–171	60	$C_{17}H_{15}N_3S_2$	62.9	4.7	13.5	19.9	
				B			62.8	4.6	13.3	19.7	
Va$_1$	C_6H_5-	H	*p*-Cl–C_6H_4-	242–4	66	$C_{15}H_{11}ClN_4S$	57.4	3.4	18.0		
				E			57.2	3.3	17.8		
Va$_2$	C_6H_5-	H	-$CH_2CH(CH_3)_2$	244–6	54	$C_{13}H_{16}N_4S$	59.7	6.1	21.5		
				E			60.0	6.2	21.5		
Va$_3$	C_6H_5-	H	*m*-CH_3O–C_6H_4	196–8	65	$C_{16}H_{14}N_4OS$	61.6	4.4	18.3	10.2	
				E			61.9	4.5	18.1	10.3	
Vb$_1$	*p*-CH_3O–C_6H_4-	H	*p*-Cl–C_6H_4-	236–7	88	$C_{16}H_{13}ClN_4OS$	55.3	3.9	16.5	9.5	
				A			55.7	3.8	16.3	9.3	
Vb$_2$	*p*-CH_3O–C_6H_4-	H	-$CH_2CH(CH_3)_2$	256–8	76	$C_{14}H_{18}N_4OS$	57.5	6.3	19.2	10.8	
				A			57.9	6.2	19.3	11.0	
Vb$_3$	*p*-CH_3O–C_6H_4-	H	*m*-CH_3O–C_6H_4-	266–8	74	$C_{17}H_{16}N_4O_2S$	60.3	4.7	16.7	9.3	
				T			60.0	4.7	16.5	9.4	
Vc$_1$	*p*-CH_3–C_6H_4-	H	*p*-Cl–C_6H_4-	260–1	80	$C_{16}H_{13}N_4ClS$	58.1	4.1	17.3	9.5	11.0
				A			58.4	4.0	17.1	9.7	10.9
Vc$_2$	*p*-CH_3–C_6H_4-	H	-CH_2–$CH(CH_3)_2$	255–7	79	$C_{14}H_{18}N_4S$	61.6	6.7	20.4		
				A			61.3	6.6	20.2		

Vc$_3$	p-CH$_3$– C$_6$H$_4$-	H	m-CH$_3$O–C$_6$H$_4$-	213–214 E	65	$C_{17}H_{16}N_4S$	62.5 63.0	5.0 4.9	17.5 17.3
VIa$_1$	C$_6$H$_5$-	H	p-Cl–C$_6$H$_4$-	161–2 E	73	$C_{16}H_{13}ClN_4S$	58.5 58.5	3.9 4.0	17.2 17.1
VIa$_2$	C$_6$H$_5$-	H	-CH$_2$– CH(CH$_3$)$_2$	85–7 P	44	$C_{14}H_{18}N_4S$	61.0 61.3	6.5 6.6	20.5 20.5
VIa$_3$	C$_6$H$_5$-	H	m-CH$_3$–OC$_6$H$_4$-	120–2 E	73	$C_{17}H_{16}N_4OS$	63.1 63.0	4.8 4.9	17.2 17.3
VIb$_1$	p-CH$_3$O– C$_6$H$_4$-	H	p-Cl–C$_6$H$_4$-	177–9 E	88	$C_{17}H_{15}ClN_4OS$	57.1 56.9	4.3 4.2	
VIb$_2$	p-CH$_3$O– C$_6$H$_4$	H	-CH$_2$CH(CH$_3$)$_2$	86–8 E	96	$C_{15}H_{20}N_4OS$	59.3 59.2	6.5 6.6	18.4 18.4
VIb$_3$	p-CH$_3$O– C$_6$H$_4$	H	m-CH$_3$O–C$_6$H$_4$-	145–6 E	96	$C_{18}H_{18}N_4O_2S$	60.7 61.0	5.0 5.1	16.0 15.8
VIc$_1$	p-CH$_3$– C$_6$H$_4$-	H	p-Cl–C$_6$H$_4$-	148–150 P	50	$C_{17}H_{15}ClN_4S$	59.5 59.6	4.4 4.4	16.5 16.4
VIc$_2$	p-CH$_3$– C$_6$H$_4$-	H	-CH$_2$CH(CH$_3$)$_2$	93–5 P	95	$C_{15}H_{20}N_4S$	62.8 62.5	7.0 6.9	19.3 19.4
VIc$_3$	p-CH$_3$– C$_6$H$_4$-	H	m-CH$_3$O–C$_6$H$_4$-	118–120 P	61	$C_{18}H_{18}N_4OS$	63.8 63.9	5.2 5.3	16.4 16.4

* A = Acetic acid, B = Benzene, E = Ethanol, T = Toluene and P = Petroleum ether 60–80°C.

RESULTS AND DISCUSSION

The structure of 6-thiono-1,3,5-triazine derivatives (**IVb, c**) was established on the basis of their elemental analysis (Table I) and their I.R. spectra which showed absorption bands at 3400–3250 (secondary amide and amine NH),[5] 2600–2550 (SH) and 1200–1050 cm^{-1} (C=S). These bands indicate that (**IV**) exists in tautomeric forms as shown in Scheme 1.

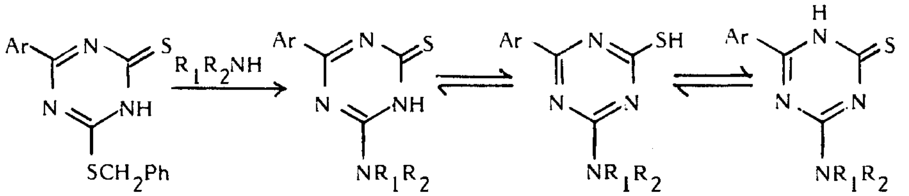


(IV)

(Scheme 1)

The formation of (**IVb, c**) in good yields by the reaction of *s*-benzylthiouronium chloride with (**II**) in presence of aqueous sodium hydroxide indicates that the amino group of *s*-benzylthiouronium chloride attacks exclusively the C=S of compound (**II**).

When (**IVa–c**) were treated with aliphatic and/or aromatic amines, in equimolar ratio, replacement of benzylthiol group by an amino group takes place to give 4-aryl-2-substituted-amino-1,6,-dihydro-6-thiono-1,3,5-triazines (**V**). This is a typical nucleophilic displacement reaction at the highly electron-deficient C_2.

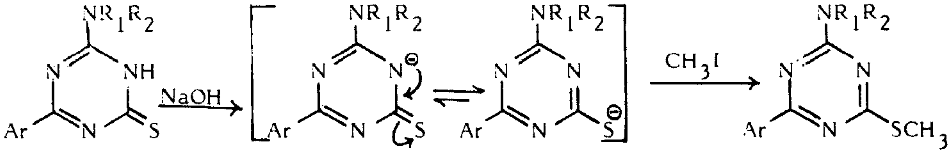


(Va-c)

(Scheme 2)

The structure of (**V**) was confirmed by its elemental analysis (Table I) and I.R. spectra which showed bands at 3460–3140 (secondary amide and amine NH),[6] 2610–2550 (SH) and 1200–1050 cm^{-1} (C=S) indicating that (**V**) exists in tautomeric forms as shown in Scheme 2.

When (**Va–c**) was treated with methyl iodide and sodium hydroxide gave the corresponding *s*-methyl derivative (**VIa–c**) (cf. Scheme 3).



(V) (VI)

(Scheme 3)

The structure of (**VI**) was deduced from (i) elemental analysis, (ii) i.r. spectrum which showed absence of the band characteristic of ν C=S, (iii) and from u.v. spectrum which showed a band at 260 nm (log ε_{max} 4.50) and at 252 nm (log ε_{max} 4.54).

EXPERIMENTAL

All melting points are uncorrected, I.R. spectra were recorded in KBr on a Unicam SP 1200 spectrophotometer.

4-Aryl-2-benzylmercapto-1,6-dihydro-6-thiono-1,3,5-triazines (**IV**). To a well stirred solution of S-benzylthiouronium chloride (0.01 mol) in water (10 ml) were added simultaneously an aqueous solution of NaOH (10 ml, IN) and a solution of (**II**) (0.01 mol) in dry benzene (10 ml) during 15 minutes. The organic phase acquired a deep yellow color. The reaction mixture was stirred for a further 30 minutes. A solution of NaOH (10 ml, 2N) was then added during 10 minutes, and the reaction was further stirred for 2 hours. The benzene layer was separated and extracted several times with NaOH solution (50 ml, 2N). The alkaline solution was cooled and acidified with ice-cooled aqueous sulphuric acid (2N) until pH 6 and then extracted with ether. The ethereal layer was washed with water, dried and the solvent removed under reduced pressure to give (**IV**) which was crystallised from benzene. The characteristic data of (**IVa–c**) are given in (Table I).

4-Aryl-2-substituted-amino-1,6-dihydro-6-thiono-1,3,5-triazines (**V**). To a solution of (**IV**) (0.01 mol) in absolute ethanol (40 ml) was added, during 15 minutes, a solution of an aliphatic or aromatic amine (0.01 mol) in ethanol (10 ml). The reaction mixture was heated under reflux for 4 hrs until a solid was formed. The solid was filtered off and recrystallised from a suitable solvent to give (**V**) (cf. Table I).

Action of methyl iodide on (**Va–c**); *Formation of 4-aryl-2-substituted-amino-6-methylthio-1,3,5-triazines* (**VIa–c**). Methyl iodide was dropwisely added to a stirred solution of (**V**) (0.01 mol) in sodium hydroxide solution (0.5 N) and ethanol (50 ml). The reaction mixture was heated gently on a water-bath for 2 hrs, then was further stirred at room temperature for 6 hrs. The reaction mixture was poured onto water and the solid formed was filtered off and recrystallised from a suitable solvent to give (**VIa–c**). The characterization data of (**VIa–c**) are shown in Table I.

REFERENCES

1. J. Goerdeler and J. Neuffer, *Chem. Ber.*, **104**, 1580 (1971).
2. G. E. M. Moussa, M. E. Shaban, A. F. Elkafrawy, A. Al-Nagdy and A. A. Saad, *Oriental J. Chem.*, Vol. 3, No. 1, 1987, pp. 61–65.
3. D. T. Elmore, J. R. Ogle, W. Fletcher and P. A. Toseland, *J. Chem. Soc.*, 4458 (1956).
4. G. D. Durant, *J. Chem. Soc.*, **92** (1967).
5. L. J. Bellamy, The infrared spectra of complex molecules, (Chapmann and Hall London), (1975).