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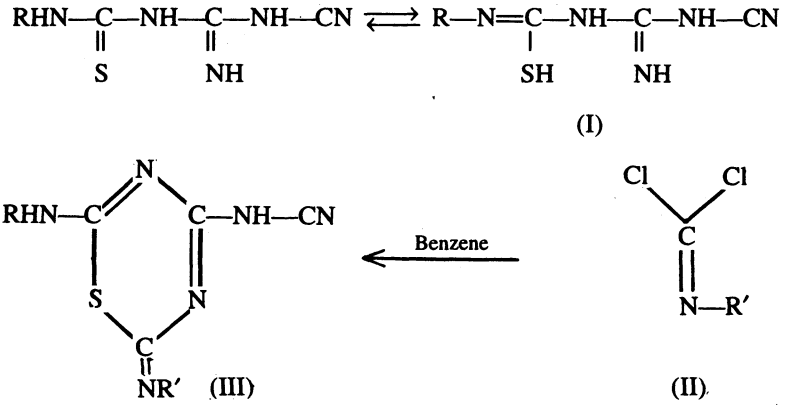
NOTE

Synthesis of 1,3,5-Thiadiazines from Some Cyanoamidino Arylthiocarbamide

D.T. TAYADE
Department of Chemistry
S.R.R.L. Science College, Morshi, Amravati-444 905, India

2-Arylamino-4-cyanoamino-6-arylimino-1,3,5-thiadizines(III) have been synthesised by the interaction of cyanoamidinoaryl thiocarbamide(I) with arylisocyanodichlorides(II) in benzene medium. Their structure have been supported on the basis of usual chemical transformations and spectral data.

Aryl/alkylisocyanodichlorides are used as intermediate for the synthesis of varieties of organic compounds[1, 2]. Pathe[3, 4] and others[5] have extensively explored the application of aryl/alkylisocyanodichloride in the synthesis of several 5 and 6-membered nitrogen and sulphur containing heterocyclic rings with special reference to 1,3-isoimidazolines, 1,3,5-thiadiazolines, 1,3,5-thiadiazines, 1,3,5-dithiazines and 1,3,5-triazines. Thus it is interesting to explore the synthetic applications, of N-aryl/alkylisocyanodichlorides with different cyanoamidino-arythiocarbamides in benzene medium to produce some 2-arylamino-4-cyano-amino-6-arylimino-1,3,5-thiadiazines.



where R = phenyl, -*p*-Cl-phenyl, -tertbutyl, -ethyl, -methyl,

R′ = phenyl, -*p*-Cl-phenyl.

All chemicals used were of pure analytical grade as required. (1) cyanoamidinophenylthiocarbamide, (2) cyanoamidino-*p*-Cl-phenylthiocarbamide, (3) cyanoamidinotertbutylthiocarbamide, (4) cyanoamidinoethylthiocarbamide and (5) cyanoamidinomethylthiocarbamide were successfully synthesised by the

interaction of different aryl/alkylisothiocyanates with cyanoguanidine in acetone medium. Aryl/alkylisothiocyanodichloride[6] has been prepared by the interaction of excess chlorine and alkyl/arylisothiocyanates.

2-Phenylamino-4-cyanoamino-6-phenylimino-1,3,5-thiadiazine (hydrochloride) (1a): Interaction of cyanoamidinophenylthiocarbamide (7.14 g, 0.02 M) with phenylisocyanodichloride (4 g, 0.02 M) in dry benzene (40 mL) was carried out. Brisk reaction with evolution of hydrogen chloride was noticed. The reaction mixture was refluxed for 4 h on water bath,. The excess of benzene was removed by distillation. The blackish dark yellow sticky product was isolated which, on trituration with petroleum ether several times gave dark yellow product (67%), m.p. 83°C (d) (Found C, 52.82; H, 2.37; N, 22.83; S, 8.72; Cl, 9.23. Required C, 53.78; H, 3.64; N, 23.52; S, 8.96; Cl, 10.08.)

IR (KBr): ν_{max} (cm^{-1}) 670(s) (C—S-stretching), 720(s) (ring C—S—C band), 1350(s) (C—N stretching, 1470(m) (C=N stretching), 1660(m) (C=NH imino), 2770(m) (CN aliphatic sym. stretching).

The product was found to be acidic in nature. It is insoluble in benzene and in acetone. The product can be desulphurisable by alkaline plumbite solution and slightly soluble in warm alkali. Similarly 1 a-j were synthesised and presented in Table-1.

TABLE-1 [(1a–j)*]

S. No.	R	R′	Yield (%)	m.p. (°C)
1 a	-phenyl	-phenyl	67	83 (d)
b	-*p*-Cl-phenyl	-phenyl	72	85 (d)
c	-tertbutyl	-phenyl	58	78 (d)
d	-methyl	-phenyl	70	72
e	-ethyl	-phenyl	71	81 (d)
f	-phenyl	*p*-Cl-phenyl	71	84 (d)
g	-*p*-Cl-phenyl	*p*-Cl-phenyl	73	73 (d)
h	-tertbutyl	*p*-Cl-phenyl	67	68 (d)
i	-methyl	*p*-Cl-phenyl	63	58 (d)
j	-ethyl	*p*-Cl-phenyl	64	63 (d)

*All compounds gave satisfactory C, H, N, S and Cl analyses.

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