

NOTE

Synthesis of Some New 2-Cyanoamino-4-Thio-5 and 6-substituted-Amino 4,5-Dihydro-S-Triazines, Part I

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In the present work, synthesis of some 2-cyanoamino-4-thio, 5 and 6-substituted amino 4,5-dihydro S-triazines are described.

S-Triazines and their derivatives have their own identity in heterocyclic compounds due to their several useful activities.¹ So a direct synthetic procedure for certain S-triazines was reported. The reactions of newly synthesised cyanoamidinosubstituted thiocarbamides(I)² were carried out with alkyl/arylisocyanodichlorides (II)³ in benzene medium afforded initially 1,3,5-thiadiazines (III) which were successfully isomerised into S-triazines (IV).

2-Cyanoamino-4-methylimino-6-p-Cl-phenylamino-1,3,5-thiadiazine hydrochloride (IIIa)

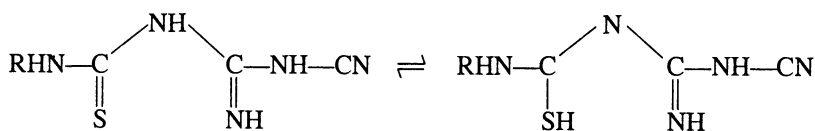
A mixture of cyanoamidino-*p*-Cl-phenyl thiocarbamide (Ia, 0.05 mL), N-methylisocyanodichloride (IIa, 0.05 mol) in benzene (40 mL) was refluxed on a water bath for 4 h. Initially vigorous reaction was set in the solution, which subsequently subsided. The excess of benzene was removed by distillation. A blackish dark brown sticky product was isolated which on trituration with petroleum ether several times gave dark yellow product (68%), m.p. 67°C (d), (C₁₁H₁₀N₆SCl₂: Found (%) C 39.28, H 2.92, N 24.78, S 9.67, Cl 20.38; Reqd. (%) C 40.24, H 3.09, N 25.60, S 9.75, Cl 21.39); R_f (dioxane) 0.3. It is unstable compound. On treatment with alkaline plumbite solution a yellow precipitate of lead mercaptide was obtained. IR ν_{max} (KBr) (cm⁻¹) 710 (ring —C—S—C— band), 1440 (thiouride corresponding to amide π bond), 1660 (—N—C= N group showing the presene of hexocyclic imino group), 2850 (CN symmetrical stretching).

Similarly, other compounds were prepared. IIIb (72%), m.p. 85°C (d); IIIc, (83%), m.p. 83°C (d); III d (75%), m.p. 72°C (d); IIIe (71%), m.p. 81°C (d), III f (58%), m.p. 78°C (d); IIIg (78%) m.p. 73°C (d); IIIh (82%), m.p. 84°C (d); III i (87%), m.p. 58°C (d); IIIj (64%), m.p. 63°C (d); IIIk (69%), m.p. 69°C (d).

2-Cyanoamino-4-thio-5-methyl-6-p-Cl-phenylamino-4,5-dihydro-S-triazine (IVa)

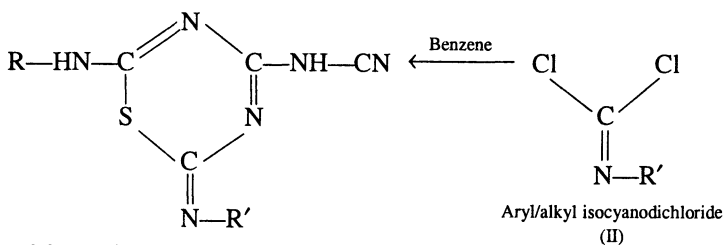
A mixture of 2-cyanoamino-4-methylimino-6-*p*-Cl-phenyl amino-1,3,5-thiazine, hydrochloride (IIIa 0.05 mol), sodium bicarbonate (2.5 g), water (50 mL) and ethanol (10 mL) was warmed on a water bath for 3 h. The resultant solid was filtered and washed with water. It was crystallised from glacial acetic acid to obtain faint yellowish crystals (78%), m.p. 185°C, C₁₁H₉N₆S: Found (%) C 44.31,

H 2.18, N 27.89, S 10.87 ; Reqd. (%) C 45.12, H 3.07, N 28.71, S 10.94) soluble in ethanol, acetone and dioxane, R_f (dioxane) 0.21, ν_{\max} (KBr) (cm^{-1}) 710 (iso form of 1,3,5-triazine ring), 1210 (p-substitution to aromatic ring), 1375 ($\text{N} \rightarrow \text{C}=\text{S}$ grouping, 1540 (N—C=N grouping), 2850 (CN sym. stretching), $\delta(\text{CDCl}_3 + \text{DMSO}-d_6)$, 1.39 [3H(CH₃)], 4.5 [2H (NH)], 7.2–7.7 [4H (Ar—H)]. Peaks at 2.3 and 3.3 are due to moisture in DMSO- d_6 .



Cyanoamidino substituted thiocarbamide
(I)

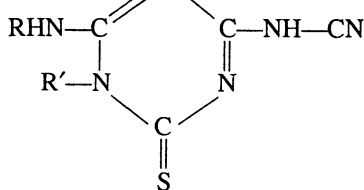
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2-Cyanoamino-4-substituted imino-6-substituted
amino-1,3,5-thiadiazine hydrochloride
(III)

Aryl/alkyl isocyanodichloride
(II)

Isomeric change
Aqueous sodium bicarbonate
in ethanol



2-Cyanoamino-4-thio-5 and 6-substituted
amino-4,5-dihydro-1,3,4-triazine
(IV)

R = -phenyl, -*p*-Cl-phenyl, -methyl,
-ethyl, -*t*-butyl
R' = -methyl, -phenyl, -*p*-Cl-phenyl

Similarly, other compounds were prepared IVb (69%), m.p. 213°C, IVc (82%), m.p. 209°C, IVd (71%), m.p. 197°C, IVe (79%), m.p. 193°C, IVf (84%), m.p. 198°, IVg (78%), m.p. 217°C, IVh (67%), m.p. 207°C, IVi (82%), m.p. 190°C, IVj (73%), m.p. 193°C; IVk (69%), m.p. 201°C.

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