Synthesis of 1-[S-TAG-Substiturtedthioamido] Dicyandiamides

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Abstract

A novel series of 1-[S-TAG-N-substiturtedthioamido]dicyandiamides (5a-f) have been synthesized successfully by refluxing tetra-O-acetyl-β-D-glucopyraosylbromide (4) with cyanoamidinosubstitutedthiocarbamides (3a-f) in 2-propanol for 3h. The structure of these newly synthesized compounds have been established on the basis of chemical characteristics, elemental analysis, IR and ^{1}H-NMR spectral analysis.

Keywords: S-Glucosylated, Tetra-O-acetyl-β-D-glucopyranosylbromide, dicyandiamides, cyanoamidinosubstituted-thiocarbamides

1. Introduction

Dicyandiamides showed noticeable pharmaceutical and biological values (Tayade D. T., 1997; Steinman, 1965). These heteroacycles were also cyclized in 5 and 6 membered heterocycles viz. thiadiazoles, dithiazoles, Hectors bases, thiadiazines and triazines. These heterocycles posses their own identity and significance in pharmaceutical, medicinal, agricultural, industrial and biotechnical sciences (Vora, 2009; El-Agrody, 2001; Hanessian, 2000; Rosowsky, A., 2004; Bamberger, 1983; Elvino Fako, 1951; Joshua, 1962; Deohate, 2005). S-glucosides and N-glucosides had been found several applications in industry and also in medicinal chemistry (Irving Goodman, 1958; Deshmukh, 1986; Umar Ali, 1985).

An exhaustive literature survey about tetra-O-acetyl-β-D-glucopyranosylbromide (Lemieux, 1963) and tetra-O-benzoyl-β-D-glucopyranosylbromide showed that these two analog play the great role in the synthesis of S-glucosylated and N-glucosylated heteroacycles and heterocycles. Very few thioglucosides of thiocarbamide were reported earlier (Bedekar, 1981).

As evident from the structure of cyanoamidinosubstitutedthiocarbamide (Tayade, 1995 & 2006), it was observed that there are various reactive sites in this molecule for the reactions. This molecule possesses –SH, -CN, -NH_2 important reactive sites for the reactions. As a wider programme of this laboratory in the synthesis of nitrogen, nitrogen and sulphur containing heteroacycles and heterocycles. The interactions of dicyandiamide with various thioureas and alkyl/arylisothiocyanates had been investigated in sufficient details in various reaction conditions (Joshua, 1962; Tayade, 1997).

Herein we report our studies on the synthesis of 1-[S-TAG-N-substiturtedthioamido]dicyandiamides (5a-f) with the interactions of tetra-O-acetyl-β-D-glucopyranosylbromide (1) with cynoamidinosubstitutedthiocarbamides (3a-f) in 2-propanol medium were investigated to isolate title compound and the structure of these newly synthesized compounds have been established on the basis of chemical characteristics, elemental analysis and IR, ^{1}H-NMR and mass spectral analysis.

2. Materials and Methods

2.1 Cynoamidinosubmethylthiocarbamides (3d)

Interaction of cyanoguanidine (0.01M) was carried out with methylisothiocyanate (0.01 M) in acetone medium on water bath for 5 hours. It was filtered in hot condition. The resultant filtrate on distillation gave needle shaped yellowish crystals. The new product was dried at room temperature and recrystallized from aqueous ethanol and identified as cynoamidinosubstitutedthiocarbamides (3d), Yield 72% m.p. 181^{0}C-183^{0}C. The reaction scheme

was shown in Scheme-I. Similarly, other compounds (3a–f) were synthesised by above mentioned method and enlisted in Table-I.

2.2 1-[S-TAG-N-phenylthioamido]dicyandiamides (5a)

1-[S-TAG-N-phenylthioamido] dicyandiamide was synthesized by refluxing a mixture of tetra-O-acetyl-*β*-D-glucopyranosylbromide (0.01M) and cyanoamidinophenylthiocarbamide (0.01M) in 2-propanol medium, on water bath for 3 hrs. During refluxing the suspended tetra-O-acetyl-*β*-D-glucopyranosylbromide and cyanoamidinophenylthiocarbamide dissolve into the solution and clear solution was obtained. It was kept for 15 Hrs. at room condition. It was then mixed with distilled water, small quantity of semisolid was obtained, it was filtered [The separated aqueous solution was acidic to litmus and gave effervesces with sodium bicarbonate solution and was not desulphurized when boiled with alkaline plumbite solution.] The aqueous solution on basification with dilute ammonium hydroxide, the resultant filtrate on distillation gave needle shaped brown crystals. The new product was dried at room temperature and recrystallized from aqueous ethanol and identified as 1-[S-TAG-N-phenylthioamido]dicyandiamides (5a), yield-78%, m. p. 167^0C. The reaction scheme was shown in Scheme-II. Similarly, other compounds (5b–f) were synthesised by above mentioned method and enlisted in Table-II.

3. Instrumentation

All the chemicals used were of Analar grade (India make). Alkyl/arylisothiocyanates were prepared according to literature method (Vogel, 1954), melting points of all synthesised compounds were determined in open capillary and uncorrected. IR-spectra were recorded on Perkin-Elmer spectrophotometer in the range 4000-400 cm^{-1} in KBr pellets. ^{1}H-NMR spectra were recorded on Bruker AC-300F spectrometer with TMS as internal standard using $CDCl_3$ and DMSO-d_6. The purity of the compounds was checked on silica gel-G plates by TLC.

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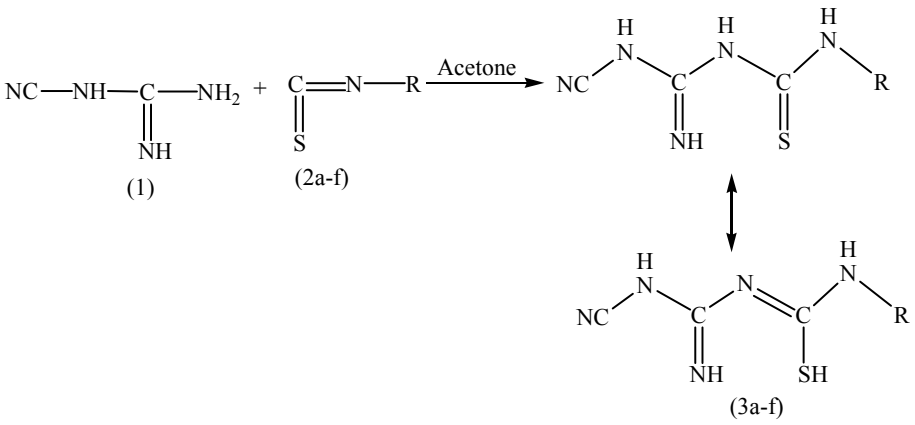
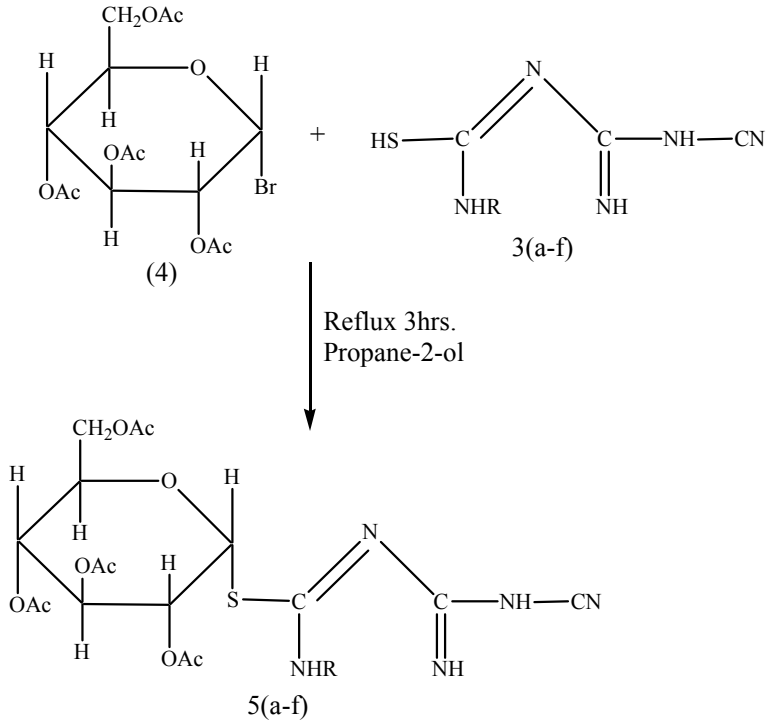
Reaction Schemes



Scheme-I



Scheme-II

Physical data for synthesised compounds

Table 1.

Compound No.	Cyanoamidinosubstitutedthiocarbamide	Yield (%)	m. p. (^{0}C)
3a	-phenyl-	72	188
3b	-p-Cl-phenyl-	67	149
3c	-p-tolyl-	63	168
3d	-methyl	72	182
3e	-ethyl-	71	189
3f	-t-butyl-	69	180

Table 2.

Compound No.	1-[S-TAG-N-**substituted**thioamido]dicyandiamide	Yield %	m.p. (^{0}C)
5a	-phenyl-	78	167
5b	-p-Cl-phenyl-	61	164
5c	-p-tolyl-	65	148
5d	-methyl-	68	161
5e	-ethyl-	64	159
5f	-t-butyl-	63	142

Table 3. Chemical data of synthesized compounds for (3a-f)

	3a		3b		3c		3d		3e		3f	
	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.
C	49.32	49.28	42.60	42.58	51.50	51.40	30.57	30.44	35.09	35.03	42.21	42.20
H	4.11	4.09	3.16	3.21	4.72	4.70	4.46	4.34	5.26	5.21	6.53	6.50
N	31.96	31.83	27.61	27.60	30.04	30.12	44.59	44.63	40.93	41.03	35.18	35.55
S	14.61	14.52	12.62	12.62	13.73	13.66	20.38	20.20	18.71	18.33	16.08	15.73
Cl			14.00	13.86								

Table 4. Chemical data of synthesized compounds for (5a-f)

	5a		5b		5c		5d		5e		5f	
	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.
C	50.27	49.98	47.30	46.70	51.24	51.20	44.35	43.12	45.51	45.63	47.63	46.32
H	4.92	4.80	4.46	4.50	4.98	4.90	5.13	4.97	5.39	5.12	5.86	5.43
N	12.75	12.22	11.99	11.89	12.46	12.00	14.37	14.34	13.97	13.23	13.23	12.44
S	5.83	5.80	5.48	5.33	5.69	5.09	6.57	6.44	6.39	6.21	6.05	5.09
Cl			6.08	6.00								

Table 5. IR spectra of synthesised compounds in (cm^{-1})

Compound	*v* (N-H)	*v* Ar-H	*v*(>C=NH)	*v*(>C≡N)	*v* (>C-N)	*v* Ph-Cl	*v* (>C-S)
(3a)	3268.6	3057.3	1653.6	2350.5	1422.4	---	737.0
(3b)	3274.2	3100.9	1629.6	2411.5	1375.7	842.6	742.3
(3c)	3304.9	3049.2	1642.5	2321.9	1365.8	---	742.6
(3d)	3195.5, 3082.1	---	1680.1	2396.2	1390.2		721.8
(3e)	3233.1, 3176.2	---	1672.4	2341.7	1333.4	---	733.7
(3f)	3219.8, 3159.3	---	1644.2	2383.5	1310.5	---	790.3
(5a)	3184.8	2931.3	1533.8,	2352.7	1324.5	---	746.2
(5b)	3290.4	3044.6	1653.6	2353.5	1321.6	810.3	740.2
(5c)	3241.3	3062.5	1642.7	2375.4	1379.5	---	713.5
(5d)	3249.6, 3184.3	---	1690.4	2378.3	1352.6		711.3
(5e)	3255.3, 3122.7	---	1623.4	2344.5	1329.4	---	741.5
(5f)	3216.3, 3119.8	---	1611.8	2367.9	1309.4	---	734.2

Table 6. NMR spectra of synthesised compounds in (ppm)

Compound	Ar-NH	Ar-H	N-H	$CO-CH_3$	C-H
(3a)	δ 8.4-7.5	δ 5.8-6.4	δ 3.9-4.5	---	---
(3b)	δ 9.4-8.1	δ 6.4-7.1	δ 3.2-3.8	---	---
(3c)	δ 8.6-7.7	δ 6.3-7.1	δ 4.0-4.5	---	δ 1.0-1.4
(3d)	---	---	δ 3.7-4.9	---	δ 0.9
(3e)	---	---	δ 4.5-4.7	---	δ 1.2-1.5
(3f)	---	---	δ 3.9-4.4	---	δ 3.97
(5a)	δ 8.9-8.1	δ 5.8-6.4	δ 4.5-4.8	δ 2.5-3.0	
(5b)	δ 9.0-8.5	δ 6.1-6.5	δ 4.3-4.9	δ 2.1-2.5	
(5c)	δ 8.7-7.8	δ 6.5-7.0	δ 4.2-4.4	δ 2.4-2.6	δ 1.2-1.5
(5d)	---	---	δ 4.0-4.6	δ 2.6-3.7	δ 1.4
(5e)	---	---	δ 4.1-4.3	δ 2.4-2.8	δ 1.3-1.7
(5f)	---	---	δ 3.8-4.2	δ 2.5-3.5	δ 4.6

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