RJC

RASĀYAN *J. Chem.*
Vol. 5 | No.2 | 173-176 | April-June | 2012
ISSN: 0974-1496 | CODEN: RJCABP
http://www.rasayanjournal.com

DEBEZYLATION AND CYCLIZATION REACTION OF CERTAIN 1-ARYL-5-HEPTA-*O*-ACETYL-β-D-MALTOSYL-2-S-BENZYL-2,4-ISODITHIOBIURETS: DIRECT SYNTHESIS OF 3-HEPTA-*O*-ACETYL-β-D-MALTOSYLIMINO-5-ARYLIMINO-1,2,4-DITHIAZOLIDINE HYDROBROMIDES

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ABSTRACT
Several 3-hepta-*O*-acetyl-β-D-maltosylimino-5-arylimino-1,2,4-dithiazolidine hydrobromides (IV a-g) have been synthezed by debenzylation and cyclization of 1-aryl-5-hepta-*O*-acetyl-β-D-maltosyl-2-*S*-benzyl-2,4-isodithiobiurets with bromine in chloroform. The identities of these newly synthesized compounds were established on the basis of elemental analysis an IR, ^{1}HNMR and Mass spectral analysis.
Keywords: Synthesis, Cyclization, Isodithiobiurets, Dithiazolidine hydrobormides.

INTRODUCITON

Maltosyl isothiocyanates[1-3] are versatile synthetic intermediates that have been used in the field of synthetic carbohydrate chemistry. The maltosylated derivatives show great potential in biological process and in medicinal chemistry. They acts as bacteriostatic agent[4] ,antifungal agent[5] and antitumour agent[6]. Synthesis of Nitrogen and Sulphur containing five and six membered heterocyclic compounds have been exhaustively investigated by several chemists[7,8] .The 1,2,4,-thiadiazoles are found highly potent as inhibitor of HIV-1[9] and shows antibiotic activity[10]. The 1,2,4-dithiazolidine have been subject of great interest because the drugs containing 1,2,4-dithiazolidine[11,12] show diverse range of physiological activites such as plant growth promoting activity , antituburculosis[13] ,anticancer and antidiabetic[14] activity . In view of applications we are interested to synthesize 3-hepta-*O*-acetyl-β-D-maltosylimino-5-arylimino-1,2,4-dithiazolidine hydrobromides (IVa-g) by debenzylation and cyclization of 1-aryl-5-hepta-*O*-acetyl-β-D-maltosyl-2-*S*-benzyl-2,4-isodithiobiurets with bromine in chloroform. The identities of these newly synthesized compounds were established on the basis of elemental analysis an IR, ^{1}HNMR and Mass spectral analysis.

EXPERIMENTAL

Melting points were taken in open capillary tubes and are found uncorrected. Optical rotations $[\alpha]^{32}_D$ were measured on Equip-Tronics EQ-800 Digital polarimeter in chloroform at 32°C. IR spectra were recorded on Perkin-Elmer RXI (4000-450 cm^{-1}) FTIR spectrometer. ^{1}HNMR were obtained on a Bruker DRX-300 NMR spectrometer at 300MHz. The samples were prepared in $CDCl_3$ with TMS as an internal reference. The mass spectra were recorded on Jeol SX-102 FAB Mass spectrometer.

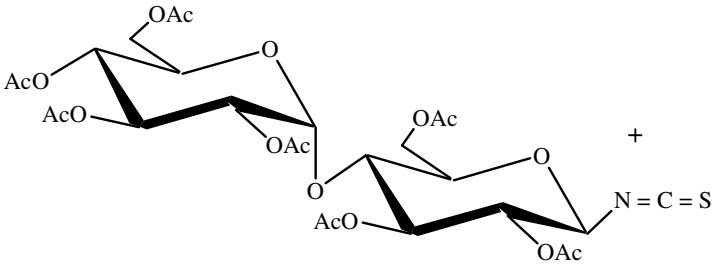
Synthesis of 1-aryl-5-hepta-*O*-acetyl-β-D-maltosyl-2-*S*-benzyl isodithiobiurets

The required 1-aryl-5-hepta-*O*-acetyl-β-D-maltosyl-2-*S*-benzyl isodithiobiurets were prepared by reported procedure[15].

Synthesis of 3-Hepta-*O*-acetyl-β-D-maltosylimino-5-phenylimino-1,2,4-dithiazolidine hydrobromide

1-Phenyl-5-hepta-*O*-acetyl-β-D-maltosyl-2-*S*-benzyl-2,4-isodithiobiurets (**4.59g, 0.005 M**) was made into paste with chloroform (5 mL) and to it was add bromine solution in chloroform (20 % Br_2 in $CHCl_3$, v/v)

drop by drop with stirring. The bromine solution in chloroform was added till evolution of lachrymatory fumes of benzyl bromide ceased. An orange red sticky mass was obtained. It was then allowed to stand for 5-6 hr. The sticky mass was washed several time with petroleum ether (60-80^{o}) and then was triturated several times with small quantity of ethanol to removed excess bromine. Some quantity of product went into ethanol, after some time it was separated out. The product obtained was acidic to litmus and recrystalise from ethanol water. On extending to other 1-aryl-5-hepta-*O*-acetyl-β-D-maltosyl-2-*S*-benzyl-2, 4-isodithiobiurets (**IIIb-g**), the related products (**IVb-g**) were isolated.

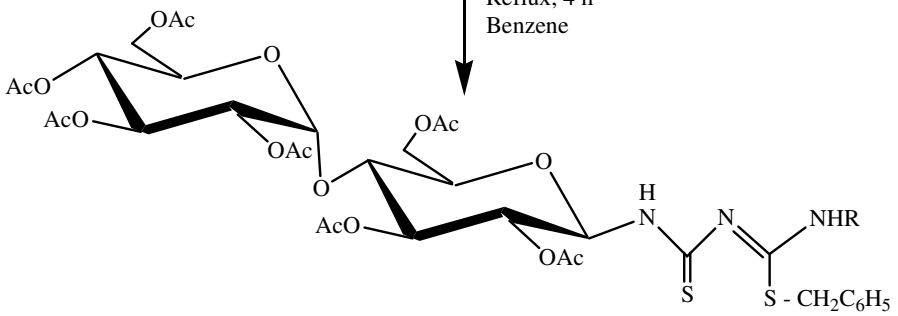


(I) (II a-g)

Hepta-*O*-acetyl-β–D-maltosyl isothiocyanate

1-Aryl-*S*-benzyl isothiocarbamide

Reflux, 4 h
Benzene

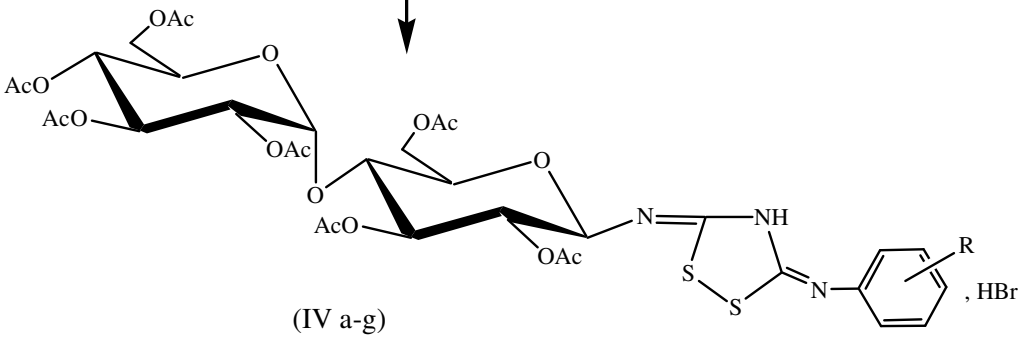


(III a-g)

1-Aryl-5-hepta-*O*-acetyl-β-D-maltosyl-2-*S*-benzyl-2, 4-isodithiobiurets

R. T. 6 h

$Br_{2\ in}\ CHCl_3$



(IV a-g)

3-Hepta-*O*-acetyl-β-D-maltosylimino-5-arylimino-1, 2, 4-dithiazolidine hydrobromide

Where, R=a) phenyl, b) *o*-Cl-phenyl, c) *m*-Cl-phenyl, d) *p*-Cl-phenyl, e) *o*-tolyl, f) *m*-tolyl, g) *p*-tolyl, Ac =$COCH_3$

Scheme-1

RESULTS AND DISCUSSION

IV(a) : 3-Hepta-*O*-acetyl-β-D-maltosylimino-5-phenylimino-1,2,4-dithiazolidine hydrobromide
Yield 73%, M.P.148^{0}C, $[\alpha]_D^{32}$+214°(c,0.2800m, $CHCl_3$), Rf-0.69 (CCl_4;EtOAc,3:2), IR (KBr)[16]: υ 3343 (N-H), 2939.5 (ali. C-H), 3343 (N-H) ,1749.8 (C=N), 1230 (C-N), 1134 (C-O), 1038.6 and 908.2 (characteristic of maltose), 600.6 cm^{-1} (C-S) ; ^{1}HNMR[17] ($CDCl_3$): δ 7.40-7.37 (d, 1H, NH), 6.82 – 7.60 (M, 5H, Ar-H), 6.17 – 6.15 (m,14 H,maltosyl ring protons); 2.3-2.0 (m, 21H,acetyl); Mass (m/z)[18] : 826 (M^+.+1), 619, 559, 168.8, 109; Anal. Calcd. for $C_{34}H_{41}O_{17}S_2N_3$; C, 49.33; H,4.95; N,5.07; S,7.73 found C, 49.03; H 4.97; N, 4.98; S, 7.81%.

IV(b) : 3-Hepta-*O*-acetyl-β-D-maltosylimino-5-*o*-Cl-phenylimino-1,2,4-dithiazolidinehydrobromide.
Yield 64%, M.P. 160^{0}C, $[\alpha]_D^{32}$+ 35.71°(c, 0.2800 m,$CHCl_3$), Rf-0.57 (CCl_4;EtOAc,3:2), IR (KBr)[16]: υ 3343 (N-H), 2969.0 (ali. C-H), 1749.3 (C=N), 1234.7 (C-N), 1134.4 (C-O), 1037.4, 937.9 and 901.4 (characteristic of maltose), 601.1 cm^{-1} (C-S) ; ^{1}HNMR[17] ($CDCl_3$): δ 7.7 - 7.6 (d, 1H, NH), 7.6 – 7.0 (M, 4H, Ar-H), 6.15 – 6.9 (m, 14H, maltose unit); 2.2 - 2.0 (m, 21H, acetyl); Mass (m/z)[18] : 861 (M^+.+1), 695.9, 168.7, 109; Anal. Calcd. for $C_{34}H_{40}O_{17}S_2N_3Cl$; C, 47.38; H, 4.64; N,4.87; S, 7.43% found C, 47.35, H, 4.60,;N, 4.80;S, 7.50%.

Table–1:Hepta-*O*-acetyl-β-D-maltosylimino-5-arylimino-1,2,4-dithiazolidine hydrobromide (IV a-g).
Reactants :(1) 1-Aryl-5-hepta-*O*-acetyl-β-D-maltosyl-2-*S*-benzyl-2,4-isodithiobiurets(III a-g) (2) Bromine in chloroform

S. No.	Products (IVa-g)	Yield (%)	M.P. (°C)	$[\alpha]_D^{32}$ ($CHCl_3$) (c, 0.2800)	Analysis		R_f (CCl_4 : EtOAc) (3:2)
					Found (%)	Required (%)	
1	IVa	73	148°C	+ 214°	N, 4.98 S, 7.81	N, 5.07 S, 7.73	0.69
2	IVb	64	160°C	+ 35.71°	N, 4.80 S, 7.50	N, 4.87 S, 7.43	0.57
3	IVc	47	171°C	+ 150°	N, 4.80 S, 7.41	N, 4.87 S, 7.43	0.48
4	IVd	56	240°C	+ 264°	N, 4.82 S, 7.41	N, 4.87 S, 7,43	0.62
5	IVe	49	243°C	- 30°	N, 4.91 S, 7.52	N, 4.99 S, 7.60	0.59
6	IVf	28	260°C	- 60°	N, 4.93 S, 7.58	N, 4.99 S, 7.60	0.61
7	IVg	58	150°C	+ 25°	N, 5.10 S, 7.64	N, 4.99 S, 7.60	0.55

Satisfactory C&H analysis was found in all cases.

IV(g) : 3-Hepta-O-acetyl-β-D-maltosylimino-5-*p*-tolylimino-1,2,4-dithiazolidine hydrobromide
Yield 58%, M.P. 150^{0}C, $[\alpha]_D^{32}$+ 25°(c, 0.2800 m, $CHCl_3$), Rf -0.55 (CCl_4;EtOAc,3:2), IR (KBr)[16]: υ 3372 (N-H), 2954.6 (ali. C-H), 1750.6 (C=N), 1231.9 (C-N), 1134 (C-O), 1036 & 905.2 (characteristic of maltose), 602.2 cm^{-1} (C-S) ; ^{1}HNMR[17] ($CDCl_3$): δ 7.7- 7.6 (d, 1H, -NH), 7.6 – 7.0 (M, 4H, Ar-H), 6.15 – 6.9 (m, 14H, maltose unit); 2.2 - 2.0 (m, 21H, acetyl protons); Mass (m/z)[18] : 841 (M^+), 695, 168.7, 109; Anal. Calcd. for $C_{35}H_{43}O_{17}S_2N_3$; C, 49.94; H, 5.11; N, 4.99; S, 7.60% found C, 49.60; H, 5.07; N, 5.10; S, 7.64%.

ACKNOWLEDGEMENTS

Authors are thankful to SAIF, C.D.R.I. Lucknow for providing spectral data and also Dr. S.G. Bhadange, Principal, Shri Shivaji College, Akola for providing all the necessary facilities.

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[RJC-936/2012]