REACTION OF ACETOPHENONE (HEPTA-*O*-ACETYL-β-LACTOSYL)THIOSEMICARBAZONES WITH ETHYL BROMOACETATE

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Abstract. Reaction of substituted acetophenone (hepta-*O*-acetyl-β-lactosyl)thiosemicarbazones with ethyl bromoacetate was performed in the presence of anhydrous sodium acetate using microwave-assisted heating method. The reaction yields were 64-80%. Structure of 2-iminothiazolidin-4-one products was confirmed by spectroscopic methods. Isomer ratios **2** and **2'** were determined by ^{1}H NMR.

It's well known that 4-thiazolidinones possess antibacterial [1], antifungal [2], antiviral [3], and antituberculosis [4], anthelmintic [5], anti-HIV [6] activities, so these compounds are interested organic chemists in synthesis. Consequently, a large number of synthetic protocols leading to these compounds have been reported in the literature [7]. As usual, the 2-imino-thiazolidinones were obtained by condensation of thiourea with chloroacetyl chloride in the presence of triethylamine in $CHCl_3$ at room temperature or ethyl bromoacetate in the presence of anhydrous sodium acetate at reflux [8]. Continuing the previous works [9], we reported herein the synthesis of some 2-iminothiazolidin-4-one compounds from corresponding acetophenone hepta-*O*-acetyl-β-lactosyl thiosemicarbazones.

In order to study on reactivity of thiosemicarbazone group, which consist of thiourea and imine bonds, we performed the reaction between substituted acetophenone hepta-*O*-acetyl-β-lactosyl thiosemicarbazones and ethyl bromoacetate performed (Scheme 1). This is the characteristic reaction of thiourea bond, as our previous studies indicated [9]. Based on the results of previous investigations about the influences of base catalyst and the nature of solvents to reaction, we have chosen anhydrous sodium acetate to be a catalyst and anhydrous chloroform to be a solvent and performed the reaction using microwave-assisted heating method (Scheme 1).

Yields of obtained pairs of 2-iminothiazolidin-4-one compounds **2**/**2'** were relative high, from 64% to 80%. 2-Iminothiazolidin-4-ones **2**/**2'** were white or pale yellows solids, having high melting points, and soluble in organic solvents (such as ethanol, methanol, dichloromethane, chloroform, toluene, benzene, ethyl acetate, acetone). The ^{1}H NMR (and ^{13}C NMR) spectra showed that obtained products were isomeric mixture. We realized that these isomers couldn't seperated out by using chromatographic method. The ratios of 2-iminothiazolidin-4-ones **2** and **2'** could be obtained from ^{1}H NMR (Table 2), changing from 69/31 to 76/24 (%).

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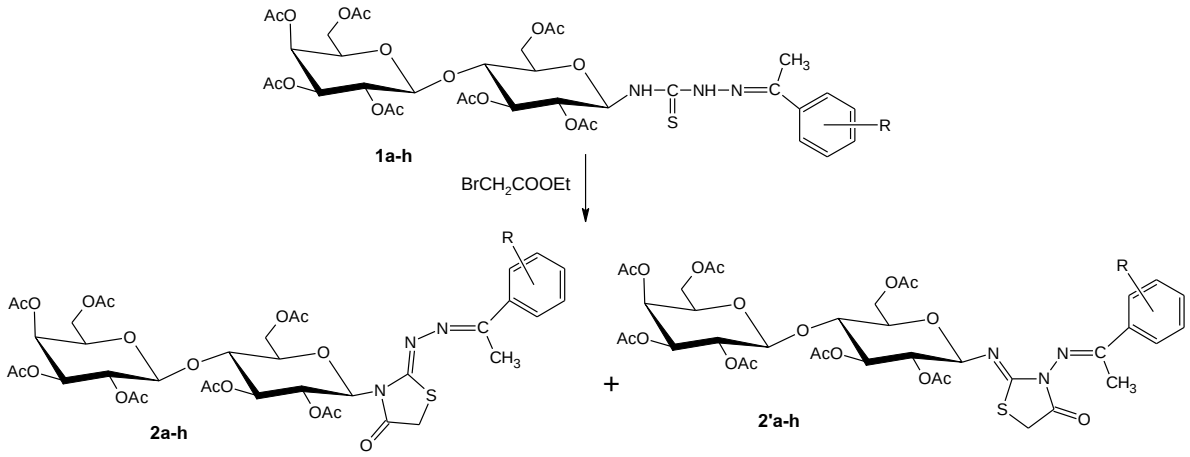

Scheme 1. Conversion of acetophenone hepta-*O*-acetyl-β-lactosyl thiosemicarbazones into 2-iminothiazolidin-4-one compounds.

The formation of 2-iminothiazolidin-4-ones **2/2'** could be preliminarily confirmed by using IR spectroscopic method. In spectra of 2-iminothiazolidin-4-ones **2/2'**, the disappearance of absorption band at 1610–1602 cm^{-1} (weak bands) which is characteristic for imine bond C=N, and apprearance of absorption band at 1619–1602 cm^{-1} (medium bands) which is characteristic for C=O bond of lactam. Other absorption bands which belong to acetate group and benzene ring, in general, were only shifted insignificantly. From ^{1}H NMR spectra, we found that reaction of thiosemicarbazones **1a-h** with ethyl bromoacetate gave the mixture of two isomers (Table 1). Ratios of these isomers were changed independing on the nature of substituent on benzene ring, and essentially, isomer **2** always predominated over.

Table 1. 2-Iminothiazolidin-4-ones **2/2'** from substituted acetophenone (hepta-*O*-acetyl-*β*-lactosyl)thiosemicarbazones **1a-h**

Entry	R	mp (ºC)	Yield, %	Ratio of 2/2', %*	IR Spectra (cm^{-1})			
					$\nu_{C=O}$	$\nu_{C=N}$	ν_{COC}	Other ν
2a/2'a	4-NO_2	148–150	72	69/31	1760	1602	1218,1071	1590,1523
2b/2'b	4-Cl-3-NO_2	127–128	75	71/29	1755	1617	1227,1056	1590,1542
2c/2'b	4-OCH_3-3-NO_2	135–137	68	68/32	1749	1615	1224,1048	1590,1532
2d/2'd	4-CH_3-3-NO_2	136–138	64	70/30	1760	1614	1221,1046	1579,1529
2e/2'e	4-Cl	110–111	79	76/24	1750	1612	1226,1049	1590,1490
2f/2'f	H	120–121	76	66/34	1762, 1735	1619	1228,1070	1585,1500
2g/2'g	2-OH-5-CH_3	119–120	80	69/31	1751	1608	1233,1051	1590,1490
2h/2'h	4-OCH_3	134–136	68	71/29	1750	1611	1227,1050	1514,1490

*) Calculatred from ^{1}H NMR spectra.

IR spectra show the characteristic absorption bands at 1762–1735 cm^{-1} ($\nu_{C=O}$ ester), 1619–1602 cm^{-1} ($\nu_{C=O}$ lactam), 1590–1480 cm^{-1} ($\nu_{C=C}$), 1233–1218 and 1071–1046 cm^{-1}

(ν_{COC} ester). The evidences that confirm the success of reactions are the absence chemical shifts at δ 10.7–10.9 ppm (singlet, NH-2) and δ 8.5–8.6 ppm (doublet, NH-4) (in ^{1}H NMR spectra). Other evidence is the disappearance of C=S signals at at δ 179.4–179.3 ppm, and the appearance of C=O (lactam) signals at δ 171.6–171.5 ppm (in ^{13}C NMR spectra). The ^{1}H NMR and ^{13}C NMR spectral elucidations of these products indicated the presence of two isomers in each obtained product. Tables 3 and 4 showed ^{1}H NMR and ^{13}C NMR spectral data for only isomer **2a-h**, and for isomer **2'a-h**. The ESI-MS spectra of 2-iminothiazolidin-4-ones **2/2'** had molecular peaks, often $[M+H]^+$ or $[M+Na]^+$ peaks, with high intensity, and in general were base peaks.

In brief, we have given the microwave-assisted synthetic method of 2-iminothiazolidin-4-one compounds from thiosemicarbazones. The spectral data (IR, ^{1}H NMR, ^{13}C NMR and MS) confirmed the structures of 2-iminothiazolidin-4-ones **2/2'** synthesized from substituted acetophenone hepta-*O*-acetyl-*β*-lactosylthiosemicarbazones.

Experimental

Melting points were determined by open capillary method on STUART SMP3 instrument (BIBBY STERILIN-UK) and are uncorrected. IR spectra (KBr disc) were recorded on a Impact 410 FT-IR Spectrometer (Nicolet, USA). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance Spectrometer AV500 (Bruker, Germany) at 500.13 MHz and 125.77 MHz, respectively, using DMSO-d_6 as solvent and TMS as an internal standard. Substituted acetophenone hepta-*O*-acetyl-β-D-lactosyl thiosemicarbazones **1a-h** were synthesized by method described in previous paper [8].

General procedure for conversion of substituted acetophenone tetra-O-acetyl-β-D-glucopyranosyl thiosemicarbazones (1) into 2-iminothiazolidin-4-one compounds (2/2'). To a suspension mixture of per-O-acetyl-β-lactosyl thiosemicarbazone **1** (2.5 mmol) and anhydrous sodium acetate (0.5 g) in dried chloroform (35 mL) was added ethyl bromoacetate (0.42 mL). Reaction mixture was irradiated in domestic microwave oven for 30–40 min. Solvent then was removed under reduced pressure; the residue was successively triturated with hexane, water and the obtained solid was filtered and washed with water, recrystallized in 96% ethanol to afford the title 2-iminothiazolidin-4-one compounds **2/2'**.

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Table 2a. ^{1}H NMR Spectra of 2-iminothiazolidin-4-ones (**2a-h**) từ acetophenon hepta-*O*-acetyl-*β*-lactosylthiosemicarbazones **1**

R	4-NO_2	4-NO_2	4-Cl-3-NO_2	4-Cl-3-NO_2	4-OCH_3-3-NO_2	4-OCH_3-3-NO_2	4-CH_3-3-NO_2	4-CH_3-3-NO_2
Proton	**2a**	**2'a**	**2b**	**2'b**	**2c**	**2'c**	**2d**	**2'd**
CH_3C=N	2.53,s	2.53,s	2.45,s	2.45,s	2.47,s	2.47,s	2.56,s	2.56,s
H-2'''	8.11,d,8.5	8.11,d,8.5	8.44,d,1.75	8.44,d,1.75	8.31,d,2.0	8.31,d,2.0	8.40,s	8.40,s
H-3'''	8.30,d,8.5	8.30,d,8.5	-	-	-	-	-	-
H-4'''	-	-	-	-	-	-	-	-
H-5'''	8.30,d,8.5	8.30,d,8.5	7.86,d,8.5	7.86,d,8.5	7.46,d,9.0	7.46,d,9.0	7.59,d,8.5	7.59,d,8.5
H-6'''	8.11,d,8.5	8.11,d,8.5	8.15,dd,8.5,1.75	8.15,dd,8.5,1.75	8.15,dd,9.0,2.0	8.15,dd,9.0,2.0	8.08,d,8.5	8.08,d,8.5
H-1'	5.82,d,8.5	6.05–6.00,m	5.83–5.81,m	6.05–6.04,m	5.80,d,9.0	6.10–6.00,m	5.81,d,9.0	6.05–6.00,m
H-2'	6.15,t,9.0	5.84–5.83,m	6.15,t,9.25	5.83–5.81,m	6.15,t,9.25	5.84–5.81,m	6.15,t,8.5	5.85–5.82,m
H-3'	5.39,t,10.0	5.25,t,10.0	5.39,t,9.0	5.25,t,10.0	5.38,t,8.75	5.38,t,8.75	5.38,t,9.0	5.38,t,9.0
H-4'	3.86,t,9.75	3.86,t,9.75	3.87,t,9.5	3.87,t,9.5	3.83,t,9.5	3.83,t,9.5	3.86,t,9.75	3.86,t,9.75
H-5'	4.16–4.15,m	4.16–4.15,m	4.16–4.14,m	4.16–4.14,m	4.14,dd,8.5,5.5	4.14,dd,8.5,5.5	4.14,dd,14.5,4.5	4.14,dd,14.5,4.5
H-6'a	4.39,d,11.0	4.39,d,11.0	4.38,d,11.0	4.38,d,11.0	4.38,d,11.5	4.38,d,11.5	4.38,d,11.5	4.38,d,11.5
H-6'b	4.01–4.00,m	4.01–4.00,m	4.09–4.00,m	4.09–4.00,m	4.05–3.99,m	4.05–3.99,m	4.07–4.00,m	4.07–4.00,m
H-1"	4.82,d,8.0	4.82,d,8.0	4.82,d,7.0	4.82,d,7.0	4.82,d,8.0	4.82,d,8.0	4.82,d,8.0	4.82,d,8.0
H-2"	4.88,t,9.0	4.88,t,9.0	4.88,t,9.5	4.88,t,9.5	4.88,t,9.0	4.88,t,9.0	4.88,t,9.0	4.88,t,9.0
H-3"	5.15,d,9.0	5.15,d,9.0	5.16,d,10.0	5.16,d,10.0	5.15,dd,10.0,2.0	5.15,dd,10.0,2.0	5.15,d,10.0	5.15,d,10.0
H-4"	5.25,d,3.0	5.38,d,3.5	5.25,d,3.0	5.25,d,3.0	5.24,d,2.0	5.24,d,2.0	5.24,d,3.0	5.24,d,3.0
H-5"	4.26,t,6.25	4.26,t,6.25	4.26,t,6.25	4.26,t,6.25	4.25,t,6.5	4.25,t,6.5	4.25,t,6.5	4.25,t,6.5
H-6"a	4.01–4.00,m	4.01–4.00,m	4.09–4.00,m	4.09–4.00,m	4.05–3.99,m	4.05–3.99,m	4.07–4.00,m	4.07–4.00,m
H-6"b	4.01–4.00,m	4.01–4.00,m	4.09–4.00,m	4.09–4.00,m	4.05–3.99,m	4.05–3.99,m	4.07–4.00,m	4.07–4.00,m
H-5a	4.01–4.00,m	4.01–4.00,m	4.09–4.00,m	4.09–4.00,m	4.05–3.99,m	4.05–3.99,m	4.07–4.00,m	4.07–4.00,m
H-5b	4.01–4.00,m	4.01–4.00,m	4.09–4.00,m	4.09–4.00,m	4.05–3.99,m	4.05–3.99,m	4.07–4.00,m	4.07–4.00,m
CO*CH_3*	2.11–1.91	2.11–1.91	2.11–1.90	2.11–1.90	2.11–1.90	2.11–1.90	2.11–1.90	2.11–1.90
Other proton					3.99,s,**4-OCH_3**	3.99,s,**4-OCH_3**	2.35,s,**4-CH_3**	2.35,s,**4-CH_3**

Table 2b. ^{1}H NMR Spectra of 2-iminothiazolidin-4-ones (**2a-h**) từ acetophenon hepta-*O*-acetyl-*β*-lactosylthiosemicarbazones **1**

R	4-Cl	4-Cl	H	H	2-OH-5-CH_3	2-OH-5-CH_3	4-OCH_3	4-OCH_3
Proton	**2e**	**2'e**	**2f**	**2'f**	**2g**	**2'g**	**2h**	**2'h**
CH_3C=N	2.45,s	2.45,s	2.47,s	2.47,s	2.28,s	2.28,s	2.43,s	2.43,s
H-2"'	7.88,d,8.5	7.88,d,8.5	7.88–7.86,m	7.88–7.86,m	-	-	7.83,d,9.0	7.83,d,9.0
H-3"'	7.52,d.8.5	7.52,d.8.5	7.46–7.45,m	7.46–7.45,m	6.83,d,8.0	6.83,d,8.0	7.00,d,9.0	7.00,d,9.0
H-4"'	-	-	7.46–7.45,m	7.46–7.45,m	7.17,d,8.0	7.17,d,8.0	-	-
H-5"'	7.52,d.8.5	7.52,d.8.5	7.46–7.45,m	7.46–7.45,m	-	-	7.00,d,9.0	7.00,d,9.0
H-6"'	7.88,d,8.5	7.88,d,8.5	7.88–7.86,m	7.88–7.86,m	7.51,s	7.51,s	7.83,d,9.0	7.83,d,9.0
H-2'	6.16,t,8.5	5.81–5.78,m	6.18,t,9.25	5.86–5.84,m	6.11,t,9.5	5.83–5.81,m	6.18,t,9.0	5.85–5.80,m
H-1'	5.81–5.78,m	6.05–6.03,m	5.81,d,9.25	6.02–6.00,m	5.83–5.81,m	6.05–6.03,m	5.79,d,9.0	6.04–5.95,m
H-3'	5.37,t,8.75	5.37,t,8.75	5.38,t,8.75	5.38,t,8.75	5.40,t,8.5	5.40,t,8.5	5.37,t,9.0	5.37,t,9.0
H-4"	5.24,d,3.0	5.24,d,3.0	5.24,d,3.0	5.24,d,3.0	5.25,d,3.0	5.25,d,3.0	5.24,d,3.0	5.24,d,3.0
H-3"	5.16–5.15, m	5.16–5.15, m	5.15,d,10.0	5.15,d,10.0	5.17–5.15,m	5.17–5.15,m	5.16,dd,9.5,2.5	5.16,dd,9.5,2.5
H-2"	4.87,t,9.5	4.87,t,9.5	4.88,t,9.0	4.88,t,9.0	4.88,t,9.0	4.88,t,9.0	4.88,t,9.0	4.88,t,9.0
H-1"	4.83,t,7.75	4.83,t,7.75	4.82,d,7.5	4.82,d,7.5	4.82,d,8.0	4.82,d,8.0	4.82,d,8.0	4.82,d,8.0
H-6'a	4.37,d,11.0	4.37,d,11.0	4.38,d,11.5	4.38,d,11.5	4.38,d,11.5	4.38,d,11.5	4.39,d,11.5	4.39,d,11.5
H-5"	4.26,t,6.25	4.26,t,6.25	4.25,t,6.5	4.25,t,6.5	4.25,t,6.5	4.25,t,6.5	4.25,t,6.5	4.25,t,6.5
H-5'	4.15–4.12,m	4.15–4.12,m	4.14,dd,8.5,5.5	4.14,dd,8.5,5.5	4.20–4.13,m	4.20–4.13,m	4.12,ddd,9.75,5.5,1.5	4.12,ddd,9.75,5.5,1.5
H-6"a	4.06–3.96,m	4.06–3.96,m	4.05–3.95,m	4.05–3.95,m	4.20–4.13,m	4.20–4.13,m	4.10–4.00,m	4.10–4.00,m
H-6"b	4.06–3.96,m	4.06–3.96,m	4.05–3.95,m	4.05–3.95,m	4.20–4.13,m	4.20–4.13,m	4.10–4.00,m	4.10–4.00,m
H-5a	4.06–3.96,m	4.06–3.96,m	4.05–3.95,m	4.05–3.95,m	4.05–3.99,m	4.05–3.99,m	4.10–4.00,m	4.10–4.00,m
H-5b	4.06–3.96,m	4.06–3.96,m	4.05–3.95,m	4.05–3.95,m	4.05–3.99,m	4.05–3.99,m	4.10–4.00,m	4.10–4.00,m
H-6'b	4.06–3.96,m	4.06–3.96,m	4.05–3.95,m	4.05–3.95,m	4.05–3.99,m	4.05–3.99,m	4.10–4.00,m	4.10–4.00,m
H-4'	3.85,t,9.75	3.85,t,9.75	3.85,t,9.5	3.85,t,9.5	3.87,t,9.5	3.87,t,9.5	3.85,t,9.75	3.85,t,9.75
CO*C*H_3	2.10–1.90	2.10–1.90	2.03–1.90	2.03–1.90	2.13–1.91	2.13–1.91	2.11–1.90	2.11–1.90
Other proton					12.15,**2-OH**;2.59,**5-CH_3**	12.15,**2-OH**;2.59,**5-CH_3**	3.81,**4-OCH_3**	3.81,**4-OCH_3**

Table 3. Selected ^{13}C NMR Spectra of 2-iminothiazolidin-4-ones (**2a-h**) from acetophenon hepta-*O*-acetyl-β-lactosylthiosemicarbazones **1**

R	4-NO_2	4-NO_2	4-Cl-3-NO_2	4-Cl-3-NO_2	4-OCH_3-3-NO_2	4-OCH_3-3-NO_2	4-Cl	4-Cl	4-OCH_3	4-OCH_3
Carbon	**2a**	**2'a**	**2b**	**2'b**	**2c**	**2'c**	**2e**	**2'e**	**2h**	**2'h**
C=O(lactam)	171.5	171.5	171.5	171.5	171.6	171.6	171.5	171.5	171.5	171.5
***CO*CH_3**	170.1–68.9	170.1–168.9	170.1–169.0	170.1–169.0	170.1–169.9	170.1–169.9	170.1–169.0	170.1–169.0	170.0–168.8	170.0–168.8
C=N imine	161.0	161.0	160.9	160.9	160.3	160.3	160.5	160.5	162.0	162.0
C-2	160.9	160.9	159.9	159.9	159.6	159.6	159.4	159.4	160.8	160.8
C-1'''	148.1	148.1	131.8	131.8	153.2	153.2	134.8	134.8	160.8	160.8
C-2'''	127.7	127.7	123.2	123.2	139.2	139.2	128.3	128.3	128.1	128.1
C-3'''	123.6	123.6	131.2	131.2	132.2	132.2	128.5	128.5	113.8	113.8
C-4'''	143.3	143.3	147.7	147.7	129.8	129.8	136.2	136.2	161.8	161.8
C-5'''	123.6	123.6	126.2	126.2	122.9	122.9	128.5	128.5	113.8	113.8
C-6'''	127.7	127.7	137.7	137.7	114.4	114.4	128.3	128.3	128.1	128.1
C-1''	99.6	99.8	99.6	100.2	99.6	101.5	99.6	101.9	99.6	99.7
C-1'	79.5	80.5	79.4	80.5	79.5	80.5	79.4	80.5	79.4	80.5
C-4'	75.4	76.5	75.4	76.5	75.5	76.5	75.4	76.5	75.4	75.4
C-5'	73.9	74.1	73.9	73.9	73.9	73.9	73.9	73.9	73.8	73.8
C-3'	73.0	73.0	73.0	73.0	73.0	73.0	73.0	73.0	73.0	73.0
C-3''	70.4	70.4	70.4	70.4	70.4	70.4	70.4	70.4	70.4	70.4
C-5''	69.7	69.7	69.7	69.7	69.7	69.7	69.7	69.7	69.7	69.7
C-2''	68.9	68.9	68.9	68.9	68.9	68.9	68.9	68.9	68.9	68.9
C-2'	67.3	67.4	67.2	67.2	67.3	67.3	67.2	67.2	67.3	67.3
C-4''	67.1	67.1	67.1	67.1	67.1	67.1	67.1	67.1	67.1	67.1
C-6'	62.1	62.1	62.1	62.1	62.1	62.1	62.1	62.1	62.1	62.1
C-6''	60.9	60.9	60.9	60.9	60.1	60.1	60.9	60.9	60.9	60.9
C-5	31.7	31.7	31.7	31.7	31.7	31.7	31.7	31.7	31.5	31.5
CO*CH_3*	20.5–20.2	20.5–20.2	20.5–20.2	20.5–20.2	20.5–20.2	20.5–20.2	20.5–20.2	20.5–20.2	20.5–20.2	20.5–20.2
C=N–*CH_3*	15.0	15.0	14.7	14.7	14.7	14.7	14.7	14.7	14.8	14.8
Other carbon					57.0,**4-OCH_3**	57.0,**4-OCH_3**			55.2,**4-OCH_3**	55.2,**4-OCH_3**