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Synthesis and investigation of mass spectra of 3-substituted-2-thioxo-imidazolidin-4-one derivatives

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The compounds 3-[(2, 4-disubstituted benzylidene)-amino]-2-thioxoimidazolidin-4-ones **2a, b** are prepared from cyclization of 2, 4-disubstituted benzaldehyde thiosemicarbazones **1a, b** with ethyl chloroacetate in presence of fused sodium acetate. Treatment of 3-[(2, 4)-disubstituted benzylidene)-amino]-2-thioxoimidazolidin-4-one **2** with acetic anhydride, benzyl chloride, diazonium chloride and aromatic aldehydes yielded the corresponding 1-acetyl-3-[(2, 4-diacetoxybenzylidene)-amino]-2-thioxoimidazolidin-4-one **3a**, 1-acetyl-3-[(4-*N*,*N*-dimethylaminobenzylidene)-amino]-2-thioxoimidazolidin-4-one **3b**, 1-benzyl-3-[(2, 4-disubstitutedbenzylidene)-amino]-2-thioxoimidazolidin-4-ones **4**, 3-{(2, 4-[dihydroxy]-5-arylazobenzylidene)-amino}-5-arylazo-2-thioxoimidazolidin-4-ones **5** and 3-[(4-dimethylamino-benzylidene)-amino]-5-arylidene-2-thioxoimidazolidin-4-ones **6** respectively. The mass spectral fragmentation patterns of some prepared compounds are investigated in order to elucidate the structure of the synthesized compounds.

Keywords: Imidazolidinones, thiosemicarbazones

IPC Code: Int. Cl.[8] C07D

Hydantoins a class of cyclic imides, have been demonstrated to possess good anticonvulsant property[1,2]. Depending on the nature of substitution on the hydantoin ring, a wide range of the other pharmacological properties, e.g. fungicidal[3], herbicidal[4], antitumor[5], anti-inflammatory[5], anti-HIV[6], hypolipienic[7] and antihyper-tensive[8] activity have also been identified.

Keeping these in view, 3-substituted-2-thioxo-imidazolin-4-ones **2** were prepared from the reaction of aromatic aldehydes and thiosemicarbazide to give arylthiosemicarbazone, followed by cyclization with ethyl chloroacetate in the presence of fused sodium acetate. The chemical behaviour of **2** towards acetic anhydride, diazonium chloride and aromatic aldehydes is described. The electron impact (EI) ionization mass spectral fragmentation of some synthesized compounds were described.

Results and Discussion

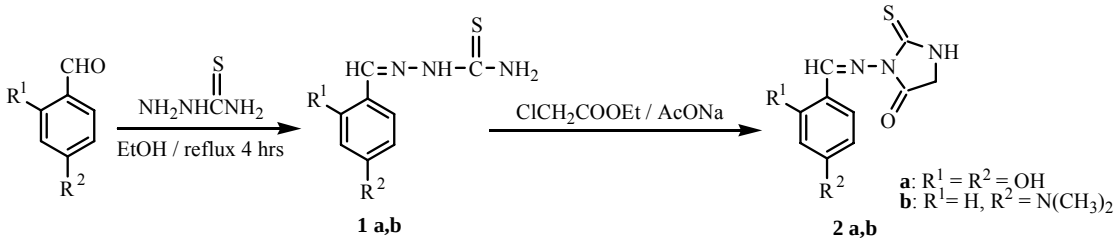
The reaction of aromatic aldehydes (such as 2,4-dihydroxybenzaldehyde and 4-*N, N*-dimethylamino-benzaldehyde) with thiosemicarbazide in ethanol under reflux gave the corresponding 2,4-disubstituted benzaldehyde thiosemicarbazones **1a,b**.

Treatment of compound **1** with ethyl chloroacetate[9] in the presence of fused sodium acetate in ethanol under reflux, yielded the corresponding 3-[(2,4-disubstituted benzylidene)-amino]-2-thioxo-imidazo-lidin-4-ones **2a,b** (**Scheme I)**.

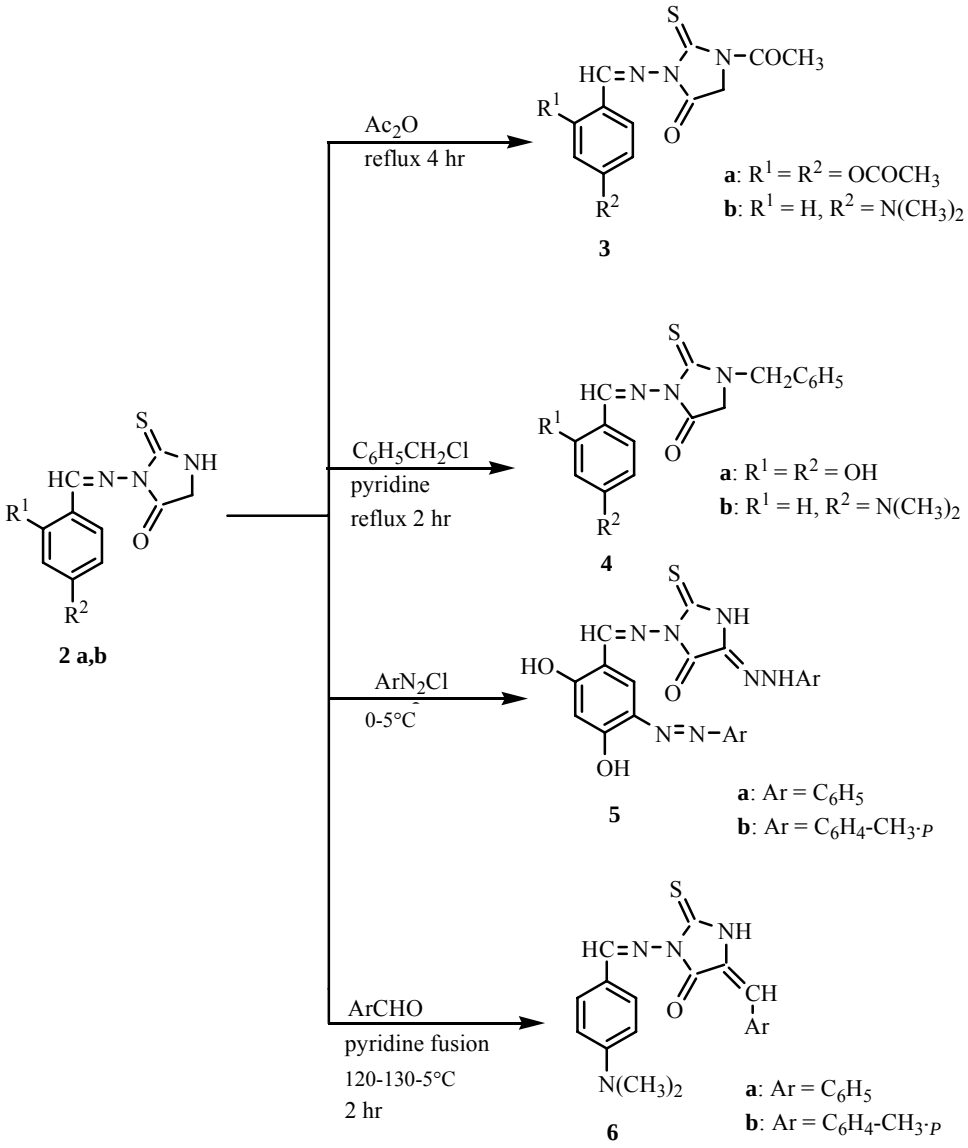
Acylation[10] of compound **2** with acetic anhydride under reflux led to the formation of 1-acetyl-3-[(2, 4-diacetoxybenzylidene)-amino]- 2 -thioxoimidazolidin-4-one **3a** and 1-acetyl-3-[(4-*N, N*-dimethylamino-benzylidene)-amino]-2-thioxo-imidazolidin-4-one **3b** (**Scheme II)**.

Alkylation of compound **2** with benzyl chloride in pyridine under reflux formed the 1-benzyl-3-[(2,4-disubstitutedbenzylidene)-amino]-2-thioxo-imidazolidin-4-ones **4a,b**.

Diazotisation of aromatic amines (such as aniline and *p*-toluidine) followed by coupling with sodium salt of 3-[(2, 4-dihydroxybenzylidene)-amino]-2-thioxo-imidazolidin-4-one **2a** gave the corresponding 3-[(2, 4-dihydroxy-5-arylazobenzylidene)-amino]-5-arylazo-2-thioxo-imidazolidin-4-ones **5a,b**. Conden-sation of compound **2b** with aromatic aldehydes (such as benzaldehyde and 4-methoxybenzaldehyde) in the presence of piperdine under fusion led to the formation of 3-[(4-dimethylaminoben-zylidene)-amino]-5-arylidene-2-thioxo-imidazolidin-4-ones **6a,b Scheme II**).



Scheme I



Scheme II

Mass spectrometry

Table I and **II** list the *m/z* (relative abundance,%) values of the principle fragment of the some synthesized compounds, while **Figures 1-5** illustrate, the mass spectra of compounds **1b, 2b, 3a, 4b** and **5a** respectively.

Compounds 1a,b: The molecular ion of compounds **1a** and **1b** fragmented further and involved two pathways as illustrated in **Table I** (**Scheme III**). The moleular ion of *m/z* 211 and 222 fragment via the pathway A to give peak at *m/z* 194 and 205 underwent fragmentaion to produce peak at

Table I — EI mass spectral data (70 eV) of compounds **1a,b** and **2a,b** *m/z* (relative intensity,%)

Compd	M^+	Pathway A		Pathway B		Other ions
		M^-	M^+	M^-	M^+	
1a	$[C_8H_9N_3O_2S]^{\bullet+}$ 211(100)	NH_3	$[C_8H_6N_2O_2S]^{\bullet+}$ 194(37.90) ↓ –NCS $[C_7H_6NO]^{\bullet+}$ 136(81.40) ↓ –CN $[C_6H_6O_2]^{\bullet+}$ 110(8.10)	NHCS	$[C_7H_8N_2O_2]^{\bullet+}$ 152(10.05) ↓ $-NH_3$ $[C_7H_5NO_2]^{\bullet+}$ ↓ –CO 135(44.90) $[C_6H_5NO]^{\bullet+}$ ↓ –CO 107(12.40) $[C_5H_5N]^{\bullet+}$ 79(17.50)	212(M^++1, 24.30), 210(7.30), 195(9.00), 153(2.60), 151(21.80), 138(13.70), 137(20.20), 134(15.40), 124(5.7), 123(15.40), 109(14.30), 108(15.90), 95(5.00), 94(12.40), 81(32.90), 80(29.50), 78(10.70), 69(22.30), 66(19 .30), 65(23.20), 63(19.30), 60(84.20), 59(23.30).
1b	$[C_{10}H_{14}N_4S]^{\bullet+}$ 222(100)	NH_3	$[C_{10}H_{11}N_3S]^{\bullet+}$ 205(53.50) ↓ –NCS $[C_9H_{11}N_2]^{\bullet+}$ 147(91.0) ↓ –CN $[C_8H_{11}N]^{\bullet+}$ 121(14.60) ↓ $-NC_2H_6$ $[C_6H_5]^{\bullet+}$ 77(16.1)	NHCS	$[C_9H_{13}N_2]^{\bullet+}$ 163(8.35) ↓ $-NH_3$ $[C_9H_{10}N]^{\bullet+}$ 146(62.40) ↓ $-N(CH_3)_2$ $[C_7H_4N]^{\bullet+}$ 102(6.80) ↓ –HCN $[C_6H_3]^{\bullet+}$ 75(4.80)	223(M^++1, 13.40), 220(5.30), 206(3.50), 191(5.60), 162(26.20), 148(15.00), 145(75.90), 132(13.10), 131(9.60), 119(14.60), 118(25.40), 117(11.30), 105(13.10), 104(8.40), 103(6.50), 91(17.60), 90(8.00), 89(12.50), 77(16.10), 76(18.60), 65(15.00), 63(16.20), 62(13.80), 59(19.80).
2a	$[C_{10}H_9N_3O_3S]^{\bullet+}$ 251(47.40)	$C_3H_4N_2OS$	$[C_7H_5NO_2]^{\bullet+}$ 135(100) ↓ $-H_2O$ $[C_7H_3NO]^{\bullet+}$ 117(59.80) ↓ –OH $[C_7H_2N]^{\bullet+}$ 100(1.30)	$C_3H_3N_2OS$	$[C_7H_6NO_2]^{\bullet+}$ 136(56.20) ↓ –HCN $[C_6H_5O_2]^{\bullet+}$ 109(15.80) ↓ –CO $[C_5H_5O]^{\bullet+}$ 81(28.00)	252(M^++1, 9.70), 234(12.00), 154(3.60), 153(5.60), 138(5.40), 122(15.90), 121(17.40), 116(4.20), 110(2.60), 108(12.20), 107(7.60), 94(42.60), 93(12.70), 80(18.20), 79(1.40), 74(11.30), 73(3.20), 69(29.5), 66(54.60), 65(36.70), 54(10.50).
2b	$[C_{12}H_{14}N_4OS]^{\bullet+}$ 262(100)	($C_3H_4N_2OS$)	$[C_9H_{10}N_2]^{\bullet+}$ 146(15.40) ↓ $-N(CH_3)_2$ $[C_7H_4N]^{\bullet+}$ 102(2.70) ↓ $-C_2H$ $[C_5H_3N]^{\bullet+}$ 77(13.10)	$C_3H_3N_2OS$	$[C_9H_{11}N_2]^{\bullet+}$ 147(66.70) ↓ –CN $[C_8H_{11}N]^{\bullet+}$ 121(2.30) ↓ $-N(CH_3)_2$ $[C_6H_5]^{\bullet+}$ 77(17.10)	263 (M^++1, 16.70), 261(3.20), 165(3.90), 164(2.20), 148(36.00), 145(22.30), 134(7.10), 133(35.70), 132(32.30), 120(5.200, 119(8.80), 118(23.20), 117(9.50), 116(2.52), 115(1.30), 91(10.90), 67(5.80), 75(3.40), 76(10.00), 59(3.80), 78(3.20).

m/z 136 and 147, corresponding to the molecular ion of 2, 4-disubstituted benzylidene radical by losing ammonia molecule.

Accordingly, the same molecular ion of *m/z* 211 and 222 fragmented via the pathway B by a cleavage hydrogen isothiocyanate to give the peak at *m/z* 152 and 163 which lost ammonia to give the peak at *m/z* 135 and 146 respectively. The base peak is the molecular ion for compounds **1a, b** is the base peak (**Figure 1**).

Compounds **2a,b**: The mass spectra (**Table I**) of compounds **2a, b** show relatively strong molecular ions and peaks typical of a cleavage or rearrangement type fragmentation. From the study of the mass spectra (**Figure 2**) of the compounds **2a,b**, it was found that the molecular ion for all these compounds fragmented further and involved two pathways as illustrated in (**Scheme IV**).

The molecular ion of compound **2b** (*m/z* 262) fragmented via the pathway A to give peak at *m/z* 146, corresponding to the molecular ion radical of

Table II — EI mass spectral data (70 eV) of compounds **3a,b** and **4a,b** *m/z* (relative intensity,%)

Compd	M^+	Pathway A		Pathway B		Other ions
		M^-	M^+	M^-	M^+	
3a	$[C_{16}H_{15}N_3O_6S]^{\bullet+}$ 377(7.60)	CH_2CO	$[C_{14}H_{13}N_3O_5S]^{\bullet+}$ 335(22.80) ↓ $-CH_2CO$ $[C_{12}H_{11}N_3O_4S]^{\bullet+}$ 293(46.80) ↓ $-CH_2CO$ $[C_{10}H_5N_4O_2S]^{\bullet+}$ 251(100.00) ↓ $-C_3H_4N_2OS$ $[C_7H_5NO_2]^{\bullet+}$ 135(65.70) ↓ $-H_2O$ $[C_7H_3NO]^{\bullet+}$ 117(48.00) ↓ $-OH$ $[C_7H_2N]^{\bullet+}$ 100(3.60)	CH_2CO	$[C_{14}H_{13}N_3O_5S]^{\bullet+}$ 335(22.80) ↓ $-CH_2CO$ $[C_{12}H_{11}N_3O_4S]^{\bullet+}$ 293(46.80) ↓ $-CH_2CO$ $[C_{10}H_9N_3O_3S]^{\bullet+}$ 251(100) ↓ $-C_3H_3N_2OS$ $[C_7H_6NO_2]^{\bullet+}$ 136(26.10) ↓ $-HCN$ $[C_6H_5O_2]^{\bullet+}$ 109(2.00) ↓ $-CO$ $[C_5H_5O]^{\bullet+}$ 81(2.80)	378(M^++1, 19.10), 336(17.90), 334(7.50), 294(8.50), 292(10.10), 277(4.70), 276(27.40), 275(12.00), 252(15.0), 250(6.80), 235(5.40), 234(35.50), 233(6.80), 209(10.80), 201(13.30), 180(14.80), 177(5.50), 159(62.40), 148(12.30), 142(14.10), 137(14.60), 116(5.10), 115(1.50), 114(7.30), 93(3.20), 65(13.00).
3b	$[C_{14}H_{16}N_4O_2S]^{\bullet+}$ 304(23.12)	CH_2CO	$[C_{12}H_{14}N_4OS]^{\bullet+}$ 262(100) ↓ $-C_3H_4N_2OS$ $[C_9H_{10}N_2]^{\bullet+}$ 146(37.20) ↓ $-N(CH_3)_2$ $[C_7H_4N]^{\bullet+}$ 102(12.35) ↓ $-HC_2$ $[C_5H_3N]^{\bullet+}$ 77(31.30)	CH_2CO	$[C_{12}H_{14}N_4OS]^{\bullet+}$ 262(100) ↓ $-C_3H_3N_2OS$ $[C_9H_{11}N_2]^{\bullet+}$ 147(68.20) ↓ $-CN$ $[C_8H_{11}N]^{\bullet+}$ 121(11.70) ↓ $-N(CH_3)_2$ $[C_6H_5]^{\bullet+}$ 77(31.30)	305(M^++1, 11.20), 261(7.20), 165(4.20), 164(9.30), 148(33.0), 145(21.60), 134(9.19), 133(45.80), 132(41.20), 120(9.20), 119(11.80), 118(27.0), 117(6.90), 116(8.30), 115(6.90), 91(13.20), 76(5.70), 75(7.30), 78(12.30), 63(11.10).
4a	$[C_{17}H_{15}N_3O_3S]^{\bullet+}$ 341(2.50)	C_7H_6	$[C_{10}H_9N_3O_3S]^{\bullet+}$ 251(100) ↓ $-C_3H_4N_2OS$ $[C_7H_5NO_2]^{\bullet+}$ 135(48.60) ↓ $-H_2O$ $[C_7H_3NO]^{\bullet+}$ 117(36.00) ↓ $-HO$ $[C_7H_2N]^{\bullet+}$ 100(1.40)	C_7H_6	$[C_{10}H_9N_3O_3S]^{\bullet+}$ 251(100) ↓ $-C_3H_3N_2OS$ $[C_7H_6NO_2]^{\bullet+}$ 136(41.40) ↓ $-HCN$ $[C_6H_5O_2]^{\bullet+}$ 109(8.00) ↓ $-CO$ $[C_5H_5O]^{\bullet+}$ 81(11.20)	342(M^++1, 1.30), 252(22.20), 250(2.80), 235(2.80), 218(1.10), 207(1.90), 204(2.70), 137(31.80), 134(1.40), 123(3.60), 122(9.50), 121(8.50), 116(4.7), 94(18.60), 93(7.40), 92(2.20), 69(12.60), 66(22.60), 65(18.20), 53(18.70), 52(13.50), 51(14.50).
4b	$[C_{19}H_{20}N_4OS]^{\bullet+}$ 352(9.81)	C_7H_6	$[C_{12}H_{14}N_4OS]^{\bullet+}$ 262(100) ↓ $-C_3H_4N_2OS$ $[C_9H_{10}N_2]^{\bullet+}$ 146(43.20) ↓ $-N(CH_3)_2$ $[C_7H_4N]^{\bullet+}$ 102(14.30) ↓ $-C_2H$ $[C_5H_3N]^{\bullet+}$ 77(29.30)	C_7H_6	$[C_{12}H_{14}N_4OS]^{\bullet+}$ 262(100) ↓ $-C_3H_3N_2OS$ $[C_9H_{11}N_2]^{\bullet+}$ 147(71.30) ↓ $-CN$ $[C_8H_{11}N]^{\bullet+}$ 121(15.20) ↓ $-N(CH_3)_2$ $[C_6H_5]^{\bullet+}$ 77(29.30)	353(M^++1, 2.70), 263(21.30), 261(4.20), 165(3.20), 164(8.20), 148(41.20), 154(17.30), 134(8.10), 133(35.80), 132(39.20), 120(10.10), 119(10.30), 118(23.00), 117(5.60), 116(9.30), 91(14.30), 90(13.20).

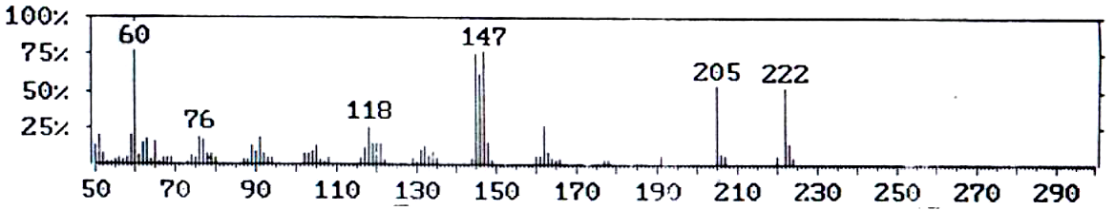


Figure 1 — Mass Spectrum (70 eV) of compound **1b**

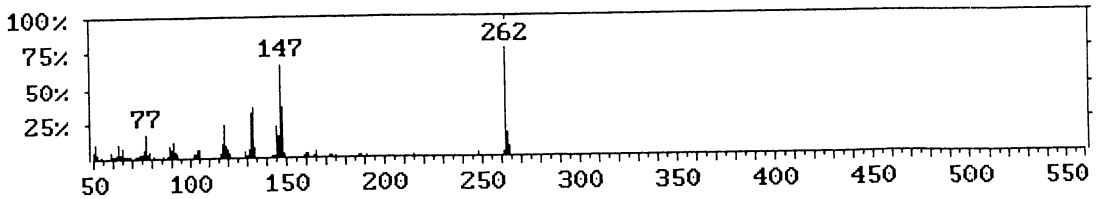


Figure 2 — Mass Spectrum (70 eV) of compound **2b**

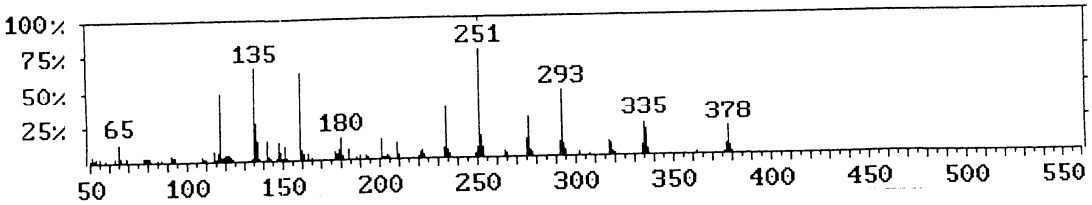


Figure 3 — Mass Spectrum (70 eV) of compound **3a**

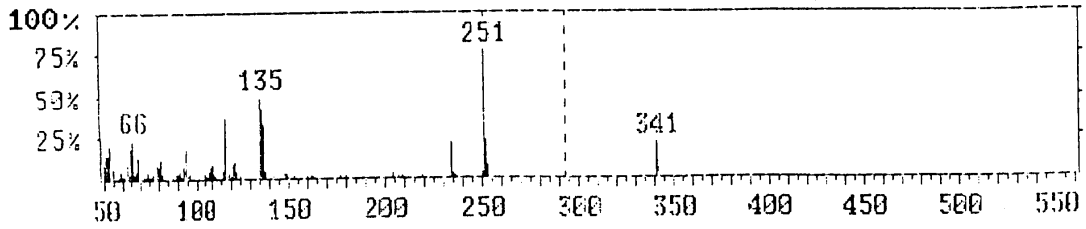


Figure 4 — Mass Spectrum (70 eV) of compound **4a**

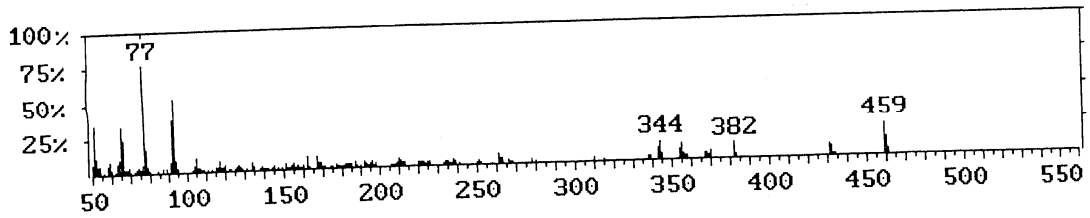
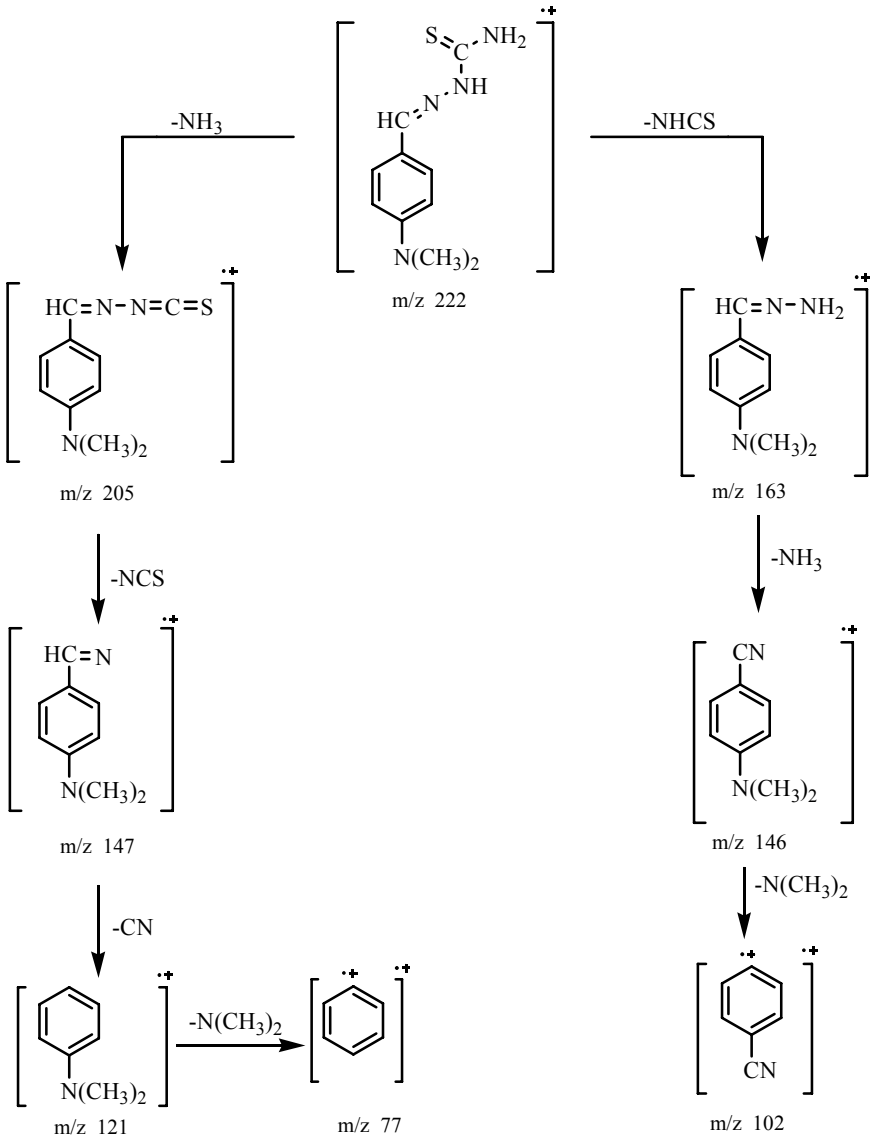


Figure 5 — Mass Spectrum (70 eV) of compound **5a**

4-dimethylamino-1-cyanobenzene. It further underwent loss of $N(CH_3)_2$, CH≡C− to give peaks at *m/z* 102 and 77 respectively.

Subsequently, the molecular ion *m/z* 262 fragmented via the pathway **B** by a cleavage of 3,4-dihydro-2-thioxo-imidazolidin-4-one radical, has relatively low abundance to give the peak at *m/z* 147, corresponding to the molecular ion radical of 4-dimethylaminobenzylidene. It further underwent loss of cyano group and $N(CH_3)_2$ to give peaks at *m/z* 121 and 77, respectively. The electron impact ionization mass spectra of compound **2b** showed a base peak of molecular ion *m/z* 262, while the base peak of compound **2a** is *m/z* 135.



Scheme III — Main pathway fragmentation pattern of compound **1b**

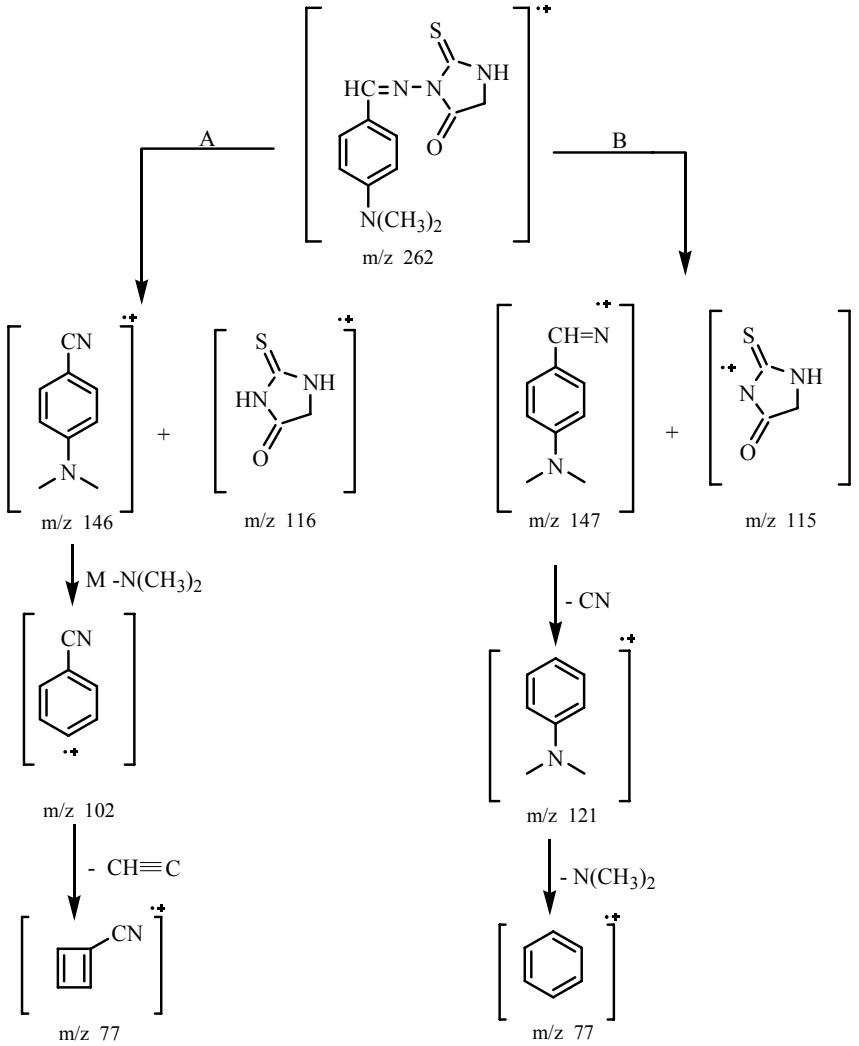
Compounds 3a,b and 4a,b: The mass spectra of compounds **3a,b** and **4a,b** (**Table II**) show relatively small molecular ions and peaks typical of a cleavage or rearrangement type fragmentation. From study the mass spectra of the compounds **3a,b** and **4a,b,** it was found that the molecular ion for all these compounds had fragmented to ions *m/z* 251 and 262, corresponding to the molecular ions of compounds **2a,b** by losing CH_2CO/or C_7H_6 groups (**Scheme V**).

The mass spectra of compounds **3a** and **4a** (**Figures 3** and **4**) gave a characteristic fragmentation pattern with a very stable fragment of *m/z* 251 which has further broken via a similar way of compound **2a**. Also, the mass spectra of compounds **3b** and **4b** give a base peak at *m/z* 262 which has further broken via a similar way of the compound **2b**.

Compounds **5a,b**: The mass spectra of compounds **5a** (**Figure 5**) and **5b** gave a characteristic fragmentation pattern with a very stable fragment of *m/z* 77 and 91. The molecular ion of *m/z* 459 and 487 fragmented further and involved various pathways (**Scheme VI**).

Experimental Section

NMR Spectra were recorded on a General Electric QE 300 instrument and chemical shifts were given with respect to TMS. IR spectra were recorded on a Perkin-Elmer 1420 spectrometer and a Biorad FTS7



Scheme IV — Main pathway fragmentation pattern of compound **2b**

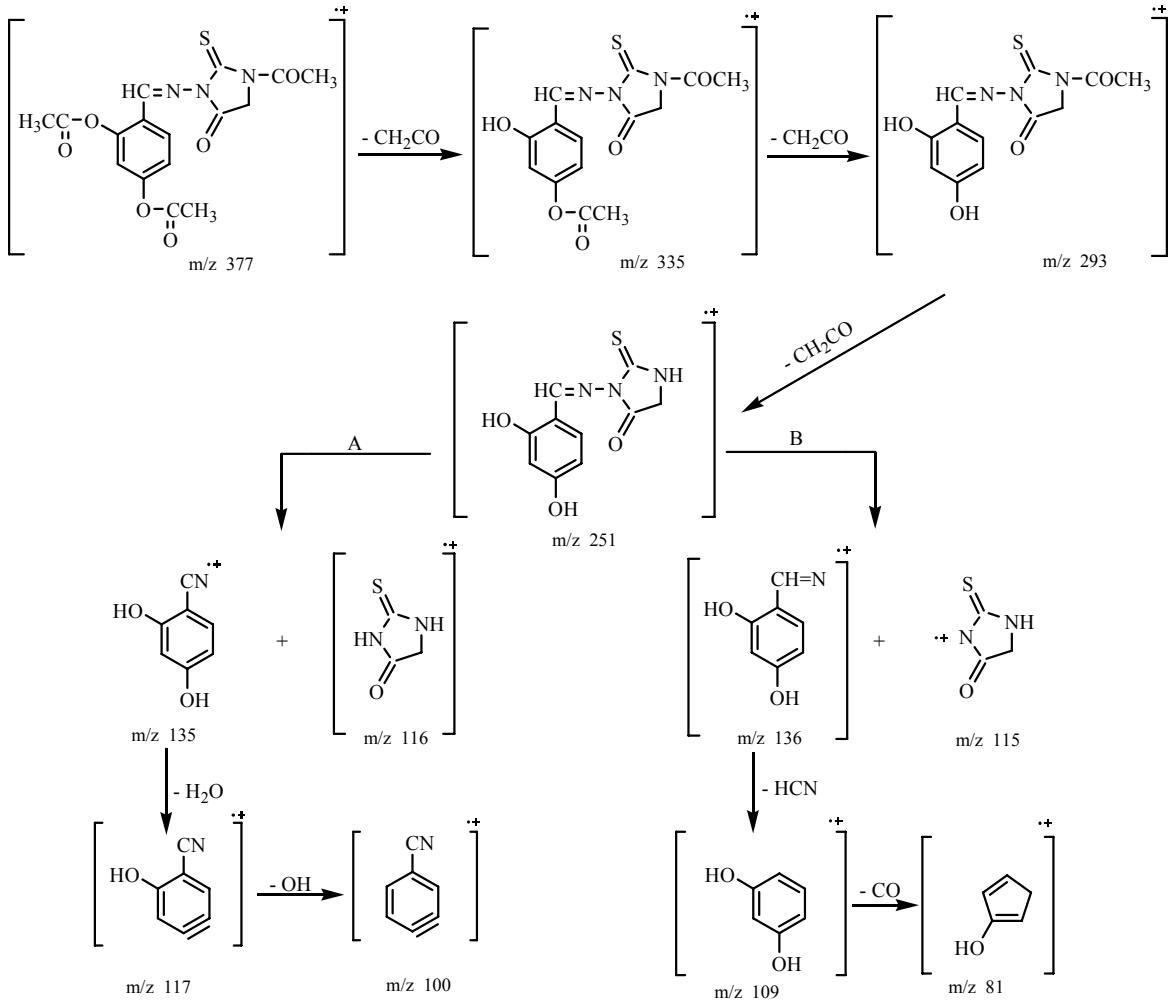
(KBr). Mass spectra were obtained on a Jeol JMS D-300 spectrometer operating at 70 eV. Microanalyses were conducted using an elemental analyzer 1106. Melting points were determined an a Reichet Hot stage and uncorrected.

2, 4-Disubstituted benzaldehyde thiosemicarbazones 1a,b: A mixture of aromatic aldehyde (0.01 mole), thiosemicarbazide (0.01 mole) in ethanol (30 mL) was heated under reflux for 4 hr, then cooled. The solid formed was filtered, dried and purified by recrystallization with ethanol to give **1**.

2, 4-Dihydroxybenzaldehyde thiosemicarbazone 1a: yield 86%, m.p. 226 °C; ^{1}H NMR (DMSO-d_6): δ 6.30 (s, 2H, NH_2), 7.26 (s, 1H, ArH), 7.30-7.51 (d, 1H, *J*=1.6 Hz, ArH), 7.58-7.81 (d, 1H, *J*=1.6 Hz, ArH), 8.21 (s, 1H, CH=N), 10.83-10.91 (br.s, 2H, OH), 11.21 (s, 1H, NH). Anal. Calcd for $C_8H_9N_3O_2S$: C, 45.49; H, 4.26; N, 19.90; S, 15.16. Found: C, 45.21; H, 4.03; N, 19.52; S, 15.01%.

4-Dimethylaminobenzaldehyde thiosemicarbazone 1b: yield 82%, m.p. 210°C; ^{1}H NMR (DMSO-d_6): δ 3.91 (s, 6H, $N(CH_3)_2$), 6.41 (s, 2H, NH_2), 7.41-7.59 (d, 2H, *J*=1.6 Hz, ArH), 7.80-7.83 (d, 2H, *J*=1.6 Hz, ArH), 8.21 (s, 1H, CH=N), 11.13 (s, 1H, NH). Anal. Calcd for $C_{10}H_{14}N_4S$: C, 54.05; H, 6.31; N, 25.23; S, 14.41. Found: C, 53.87; H, 6.09; N, 25.06; S, 14.26%.

3-[(2, 4-Disubstituted benzylidene)-amino]-2-thioxo-imidazolidin-4-ones 2a,b: A mixture of **1** (0.01 mole), ethyl chloroacetate (0.01 mole) and fused acetate (0.03 mole) in ethanol (50 mL) was heated under reflux for 4 hr, then cooled and poured into water. The resulting solid was filtered off, washed with water, dried and purified by butanol to give **2**.



Scheme V — Main fragmentation on pathway of compound **3a**

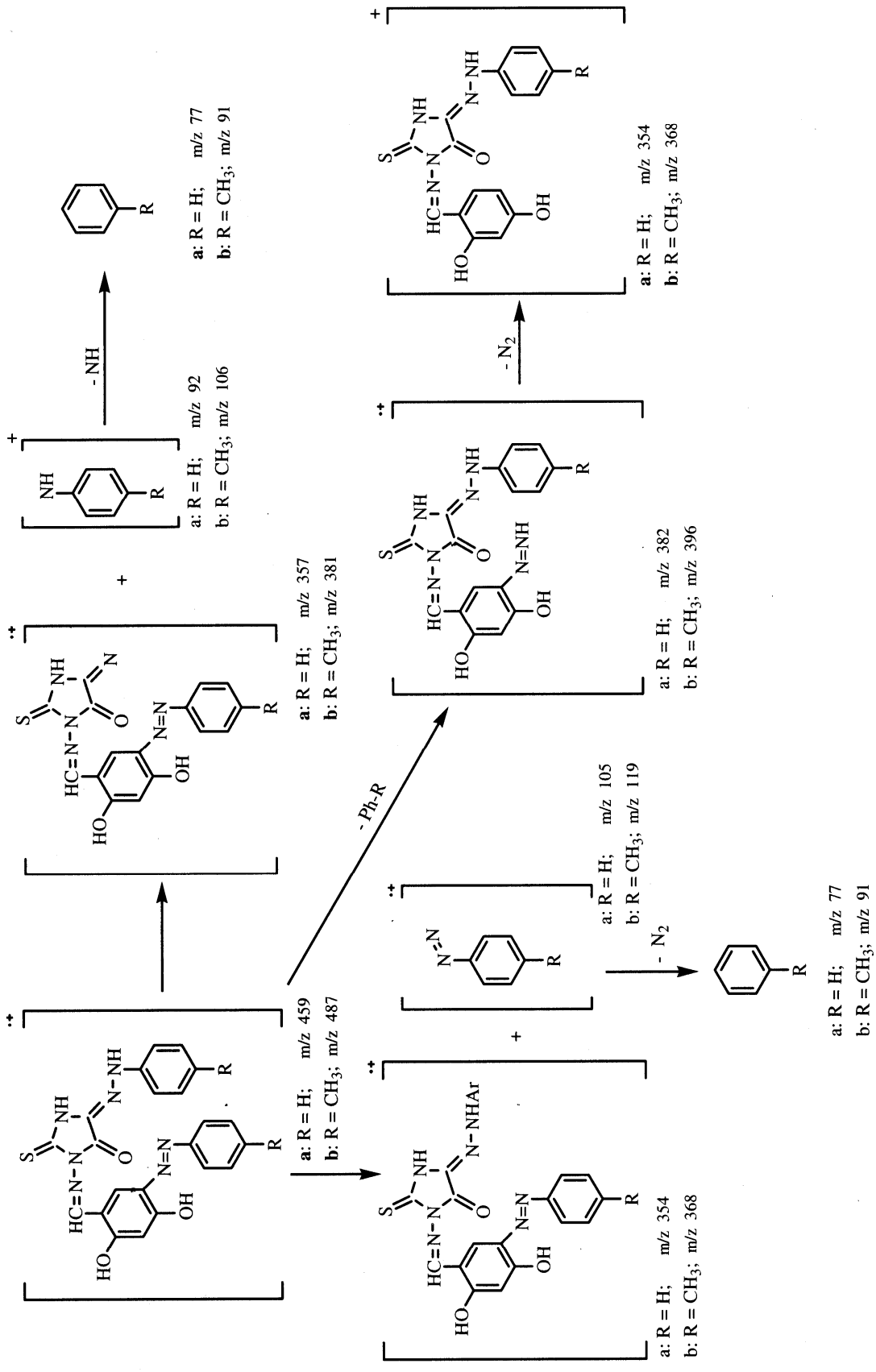
3-[(2, 4-Dihydroxybenzylidene)-amino]-2-thioxo-imidazolidin-4-one 2a: Yield 73%, m.p. 305°C; ^{1}H NMR (DMSO-d_6): δ 3.90 (s, 2H, CH_2N), 6.91 (s, 1H, ArH), 7.0-7.29 (d, 1H, *J*=1.6 Hz, ArH), 7.32-7.60 (d, 1H, *J*= 1.6 Hz, ArH), 8.31 (s, 1H, CH=N), 10.10-10.20 (br.s, 2H, OH), 11.01 (s, 1H, NH). Anal. Calcd for $C_{10}H_9N_3O_3S$: C, 47.80; H, 3.59; N, 16.73; S, 12.75. Found: C, 47.56; H, 3.32; N, 16.50; S, 12.49%.

3-[(4-dimethylaminobenzylidene)-amino]-2-thioxo-imidazolidin-4-one 2b: yield 76%; m.p. 238°C; ^{1}H NMR (DMSO-d_6): δ 2.97 (s, 6H, $N(CH_3)_2$), 3.92 (s, 2H, $NHCH_2CO$), 6.83-7.21 (d, 2H, *J*=1.6, ArH), 7.24-7.61 (d, 2H, *J*=1.6 Hz, ArH), 8.23 (s, 1H, CH=N), 10.35 (s, 1H, NH). Anal. Calcd for $C_{12}H_{14}OS$: C, 54.96; H, 5.34; N, 21.37; S, 12.21. Found: C, 54.67; H, 5.17; N, 21.13; S, 12.03%.

Reaction of 2 with acetic anhydride. Formation of 3a,b: A solution of **2** (0.01 mole) in acetic anhydride (25 mL) was heated under reflux for 4 hr, then cooled and poured onto ice-water. The resulting product was filtered off, washed with water, dried and purified by benzene to give **3**.

1-Acetyl-3-[(2, 4-diacetoxybenzylidene)-amino]-2-thioxo-imidazolidin-4-one 3a: yield 61%, m.p. 203°C; ^{1}H NMR ($CDCl_3$): δ 2.04 (s, 3H, $COCH_3$), 2.30 (s, 6H, 2 × $COCH_3$), 4.30 (s, 2H, NCH_2CO), 6.90 (s, 1H, ArH), 7.12-7.31 (d, 1H, *J*=1.6 Hz, ArH), 7.36-7.71 (d, 1H, *J*=1.6 Hz, ArH), 8.11 (s, 1H, CH=N); Anal. Calcd for $C_{16}H_{15}N_3O_6S$: C, 50.93; H, 3.98; N, 11.14; S, 8.49. Found: C, 50.68; H, 3.74; N, 11.02; S, 8.21%.

1-Acetyl-3-[(4-dimethylaminobenzylidene)-amino]-2-thioxo-imidazolidin-4-one 3b: Yield 62%, m.p. 245°C; ^{1}H NMR (DMSO-d_6): δ 2.11 (s, 3H, $COCH_3$), 2.98 (s, 6H, $N(CH_3)_2$), 3.92 (s, 2H, NCH_2CO), 6.81-7.23 (d, 2H, *J* = 1.6 Hz, ArH), 7.33-7.71 (d, 2H, *J*=1.6



Scheme VI — Main fragmentation pathway of compound **5a,b**

Hz, ArH), 8.23 (s, 1H, CH=N); Anal. Calcd for $C_{14}H_{16}N_4O_2S$: C, 55.26; H, 5.26; N, 18.42; S, 10.53. Found: C, 55.02; H, 5.07; N, 18.21; S, 10.29%.

1-Benzyl-3-[(2, 4-disubstitutedbenzylidene)-amino]-2-thioxo-imidazolidin-4-ones 4a,b: A mixture of **2** (0.01 mole) and benzyl chloride (0.01 mole) in pyridine (25 mL) was heated under reflux for 2 hr, The reaction mixture was cooled and acidified with dilute hydrochloric acid (2 mole/L). The solid formed was filtered off, washed with water, dried, and recrystallized from ethanol to give **4**.

2-Benzyl-3-[(2, 4-dihydroxybenzylidene)-amino]-2-thioxo-imidazolidin-4-one 4a: Yield 63%, m.p. 280°C, ^{1}H NMR (DMSO-d_6): δ 3.32 (s, 2H, NCH_2), 3.93 (s, 2H, NCHCO), 6.81-7.78 (m, 8H, ArH), 8.31 (s, 1H, CH=N), 10.21-10.26 (br. s, 2H OH). Anal. Calcd for $C_{17}H_{15}N_3O_3S$: C, 59.82; H, 4.39; N, 12.32; S, 9.83. Found: C, 59.63; H, 4.11; N, 12.09; S, 9.58%.

Benzyl-3-[(2, 4-dimethylaminobenzylidene)-amino]-2-thioxo-imidazolidin-4-one 4b: Yield 61%, m.p. 265°C, ^{1}H NMR (DMSO-d_6): δ 2.96 (s, 6H, $N(CH_3)_2$), 3.30 (s, 2H, NCH_2-), 3.93 (s, 2H, NCH_2CO), 6.83-7.76 (m, 9H, ArH), 8.21 (s, 1H, CH=N). Anal. Calcd for $C_{19}H_{20}N_4OS$: C, 64.77; H, 5.68; N, 15.91; S, 9.09. Found: C, 64.56; H, 5.52; N, 15.59; S, 8.89%.

5-Arylazo-3-[(2,4-dihydroxy-5-arylazobenzylidene)-amino]-2-thioxoimidazolidin-4-ones 5a,b: A solution of **2a** (0.01 mole) in aqueous sodium hydroxide (50 mL, 10%) was chilled in ice to (0-5°C), A cold aqueous solution (0-5°C) of the diazonium salt (0.02 mole) was added dropwise with stirring during 45 min. After addition the mixture was stirred for further 30 min and then left for 2 hr, in a refrigerator. The precipitated product was collected, washed with water, dried and purified by recrystallization with ethanol to give **5**.

5-Phenylazo-3-[(2, 4-dihydroxy-5-phenylazobenzylidene)-amino]-2-thioxo-imidazo lidin-4-one 5a: Yield 89%, m.p. 270°C, ^{1}H NMR (DMSO-d_6): δ 6.81-7.91 (m, 12H, ArH), 8.20 (s, 1H, CH=N), 8.61 (s, 1H, NHPh), 10.11 (s, 1H, NH), 10.53-10.61 (br.s, 2H, OH); MS (*m/z*): 460(M^++1, 12.30), 459(M^+, 22.60), 383(3.60), 382 (10.90), 369(2.80), 368(4.00), 367(4.70), 358(2.80), 357 (2.30), 345(4.90), 344(13.10), 343(8.30), 315(2.20), 278(3.50), 367(2.10), 266(3.50), 262(3.8), 261(6.80), 238(4.40), 236(2.10), 235(2.70), 209 (2.70), 208(1.70), 207(7.20), 196(4.10), 195(3.10), 193(2.80), 187(4.60), 184(3.50), 177(3.10), 168(8.00), 167(8.00), 155(4.80), 154(3.30), 135 (2.90), 134(5.00), 120(3.80), 119(2.90), 118(2.70), 117(7.10), 116(2.90), 93(52.90), 92(37.00), 91(6.50), 78(16.20), 77(100), 76(5.00), 66(23.60), 65(33.70), 52(11.20), 51(34.10). Anal. Calcd for $C_{22}H_{17}N_7O_3S$: C, 57.52; H, 3.70; N, 21.35; S, 6.97. Found: C, 57.39; H, 3.55; N, 21.17; S, 6.69%.

5-*p*-Tolylazo-3-[(2, 4-dihydroxy-5-*p*-tolylazobenzylidene)-amino]-2-thioxo-imidazolidin-4-one 5b: Yield 83%, m.p. 256°C; ^{1}H NMR (DMSO-d_6): δ 2.33 (s, 6H, 2×CH_3), 6.89 (s, 1H, NH-Ar), 10.23 (s, 1H, NH), 10.16–10.66 (br. s, 2H, OH); MS (*m/z*) 488(M^++1, 11.20), 487(M^+, 23.70), 486(M^+-1, 8.30), 396(12.30) 382(2.30), 381(21.30), 369(12.30), 368(37.35), 358(3.10), 357(2.20), 345(3.90), 344(17.30), 316(3.20), 315(3.50), 378(4.30), 238 (6.30), 236(7.10), 235(2.30), 196(3.11), 195(4.21), 187(5.10), 186(3.50), 168(6.30), 167(9.30), 155(3.80), 154(7.30), 135(12.30), 134(12.30), 120 (4.80), 114(2.92), 118(6.80), 117(11.30), 116(6.30), 93(11.30), 92(23.30), 91(100), 90(16.30), 78(10.30), 77(6.30), 76(35.30), 66(20.35), 65(35.80), 52(14.60), 51(33.60). Anal. Calcd for $C_{24}H_{21}N_7O_3S$: C, 59.14; H, 4.31; N, 20.12; S, 6.57. Found: C, 59.01; H, 4.09; N, 20.01; S, 6.31%.

5-Arylidene-3-[(4-dimethylamino benzylidene)-amino]-2-thioxo-imidazolidin-4-one 6a,b: A mixture of **2b** (0.01 mole), aromatic aldehydes (such as benzaldehyde or anisaldehyde (0.01 mole) and piperdine (1 mL) was fused on a hot plate at 120-30°C for 2 hr. The reaction mixture was cooled and acidified with dilute hydrochloric acid (2*N*). The crude product was filtered off, washed with water, dried and purified by recrystallization with acetic acid to give **6**.

5-Benzal-3-[(4-dimethylaminobenzylidene)-amino]-2-thioxo-imid-azolidin-4-one 6a: Yield 76%; m.p. 250°C; ^{1}H NMR (DMSO-d_6): δ 2.95 (s, 6H, $N(CH_3)_2$), 6.79-7.81 (m, 10 H, ArH and olefinic proton), 8.23 (s, 1H, CH=N), 10.35 (s, 1H, NH); MS (*m/z*): 351(M^++1, 35.80), 350(M^+, 100), 333(18.40), 188(11.50), 185(9.00), 178(12.50), 177(57.90), 176(18.70), 164(7.20), 163(15.00), 162(16.20), 161(16.80), 160(37.40), 159(14.30), 148(53.00), 147(45.20), 146(18.70), 134(33.30), 133(78.80), 132(43.30), 129(13.70), 128(26.80), 119(10.00), 118(34.90), 117(25.50), 116(16.50), 115(28.30), 104(10.30), 102(21.50), 91(23.40), 90(23.40), 89(29.00), 78(8.10), 77(28.30), 76(8.10), 65(14.60), 63(14.30), 52(2.80), 51(37.40). Anal. Calcd for $C_{19}H_{18}N_4OS$: C, 65.14; H, 5.14; N, 16.00; S, 9.14. Found: C, 65.00; H, 5.03, N, 15.87; S, 8.97%.

5-(*p*-Methoxy)benzal-3-[(4- dimethylaminobenzylidene)-amino]-2-thioxo-imidazolidin-4-one 6b: Yield 75%, m.p. 210°C; ^{1}H NMR (DMSO-d_6): δ 2.96 (s, 6H, $N(CH_3)_2$), 3.85 (s, 3H, OCH_3), 6.79-7.81 (m, 9H, ArH and olefinic), 8.23 (s, 1H, CH=N), 10.67 (s, 1H, NH); MS (*m/z*): 380(M^+, 58.00), 367(85.40), 366(17.60), 193(16.10), 190(13.20), 177(10.70), 175(12.70), 166(16.60), 165(36.10), 164(100), 151(14.00), 150(24.40), 149(70.70), 148(44.40), 147(45.40), 135(15.60), 139(45.40), 133(38.50), 132(36.60), 122(10.70), 121(38.50), 119(35.10), 118(28.30), 107(21.50), 106(10.20), 105(16.60), 103(14.60), 102(15.60), 92(13.70), 91(33.20), 90(17.60), 89(33.20), 79(13.20), 78(26.30), 77 (53.70), 65(19.00), 64(37.10), 63(30.70), 62(22.00), 54(13.20), 53(20.00), 51(37.60), 50(14.60). Anal. Calcd for $C_{20}H_{20}N_4O_2S$: C, 63.16; H, 5.26; N, 14.74; S, 8.42. Found: C, 63.03; H, 5.10; N, 14.49; S, 8.26%.

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