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Synthesis and mass spectral fragmentation patterns of some thiazole and imidazolidine derivatives

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3-[(Thiophen-2-ylmethylene)-amino]-4-oxo-imidazolidin-2-thione **4** and 5-aryl-2-[(thiophen-2-ylmethylene)-hydrazino]-thiazole **5** have been prepared *via* cyclization of 1-(thiophen-2-ylmethylene)-thiosemicarbazone **3** with ethyl chloroacetate and ω-bromomethyl aryl ketones in presence of fused sodium acetate. Reaction of compounds **4** and **5** with hydrazine hydrate and acetic anhydride gives 1,2-bis-(thiophen-2-ylmethylene)-hydrazone **7** and N-acetyl derivatives **6** and **10**. Treatment of **4** with benzyl chloride, choloracetyl chloride and 4-chlorobenzaldehyde yields the corresponding N-benzyl derivative **8**, imidazolo [5, 1-c]-oxazine **9** and 3-[(thiophen-2-ylmethylene)-amino]-4-oxo-5-(4-chlorobenzylidene)-imidazolidin-2-thione **11**, respectively. The mass spectral fragmentation patterns of some prepared compounds have been investigated in order to elucidate the structure of the synthesized compounds.

Keywords: Synthesis, mass spectral, thiazole and imidazolidine derivatives

IPC: Int.Cl.[8] C07D

Hydantoins, a class of cyclic imides, have been demonstrated to possess good anticonvulsant properties[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], antiinflammatory[6], anti-HIV[7], hypblipienic[8], and antihypertensive[9] activity, are also displayed.

In view of this, 3-[(thiophen-2-ylmethylene)-amino]-4-oxo-imidazolidin-2-thione **4** and 5-aryl-2-[(thiophen-2-ylmethylenehydrazino]-thiazoles **5** were prepared from the reaction of ethyl β-(thiophen-2-yl)-α-cyanoacrylate **1** and thiosemicarbazide to give 1-(thiophen-2-ylmethylen)-thiosemicarbazone **3**, followed by the cyclization of **3** with ethyl chloroacetate and ω-bromomethyl aryl ketones in presence of fused sodium acetate. The chemical behavior of compounds **4** and **5** towards hydrazine hydrate, acetic anhydride, benzyl chloride, chloroacetyl chloride and 4-chlorobenzaldehyde is described. The electron impact (EI) ionization mass spectral fragmentation of some synthesized compounds is also described.

Results and Discussion

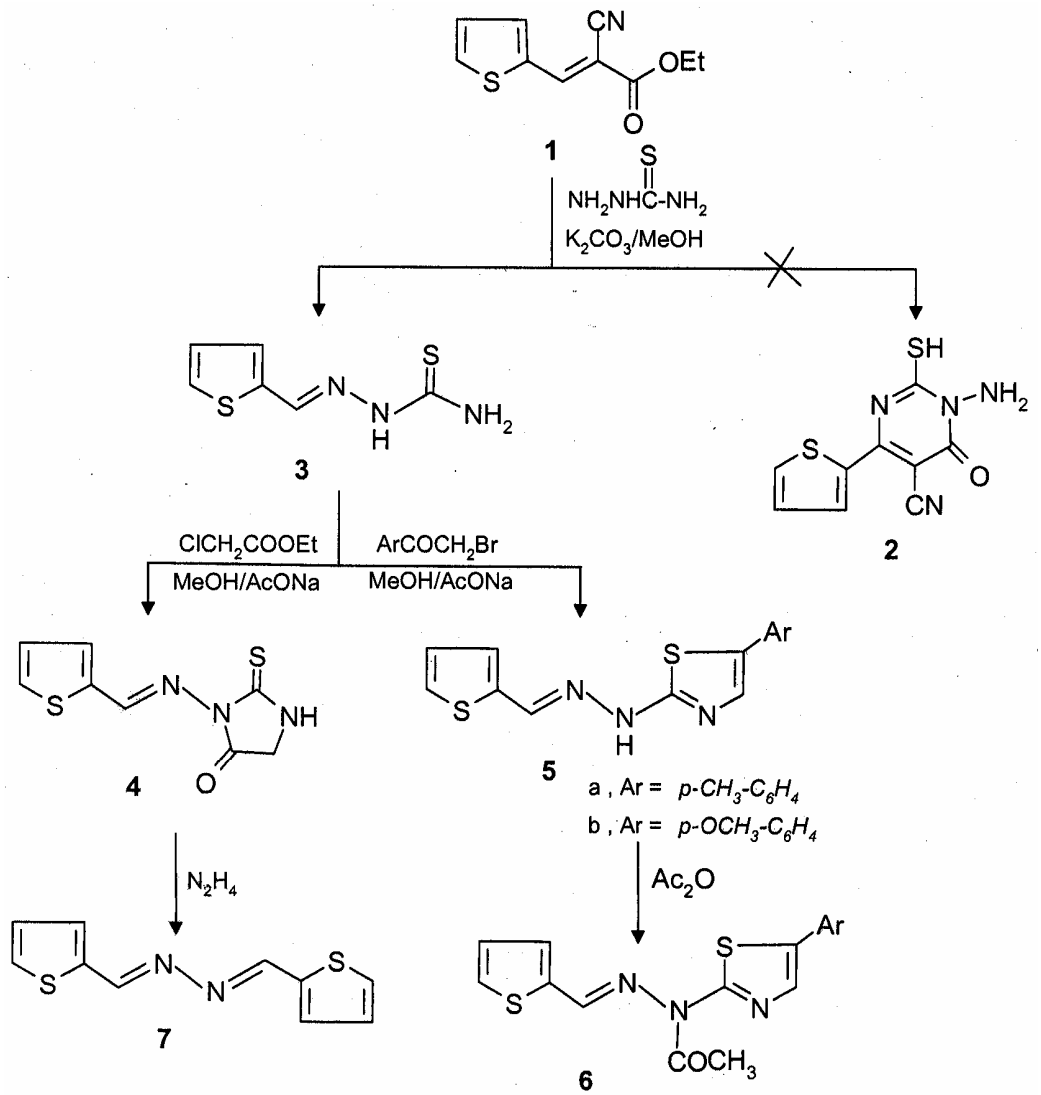
Synthesis

The reaction of ethyl β-(thiophen-2-yl)-α-cyanoacrylate **1** with thiosemicarbazide in presence of anhydrous potassium carbonate in methanol under reflux gave the corresponding 1-(thiophen-2-yl methylene)-thiosemicarbazone **3**, which does not give the expected product **2 (Scheme I)**.

Treatment of compound **3** with ethyl chloroacetate and ω-bromomethyl aryl ketones (such as 4-methyl-phenacyl bromide and 4-methoxyphenacyl bromide) in presence of fused sodium acetate in methanol under reflux, yielded the corresponding 3-[(thiophen-2-ylmethylene)-amino]-4-oxo-imidazolidin-2-thione **4** and 5-aryl-2-[(thio-phen-2-ylmethylene)-hydrazino]-thiazole **5 a, b**.

Acylation of compounds **4** and **5** with acetic anhydride under reflux led to the formation of l-acetyl-3-[(thiophen-2-ylmethylene)-amino]-4-oxoimidazolidin-2-thione **10** and 5-aryl-2-[(thiophen-2-ylmethylene)-acetylhydrazino]-thiazole **6**. The hydrazinolysis of compounds **4** and **5** with hydrazine hydrate in ethanol led to the formation of 1,2-bis(thiophen-2-ylmethylene)-hydrazone **7**, which may be formed by the nucleophilic attack at methylene carbon atom in **4** or **5** by hydrazine *via* the removal of 1-aminoimidazolidin-2-thione or 2-amino-5-arylthiazole as shown in **Scheme II**.

Alkylation of **4** with benzyl chloride in presence of triethyl amine afforded the corresponding 1-benzyl-3-



Scheme I

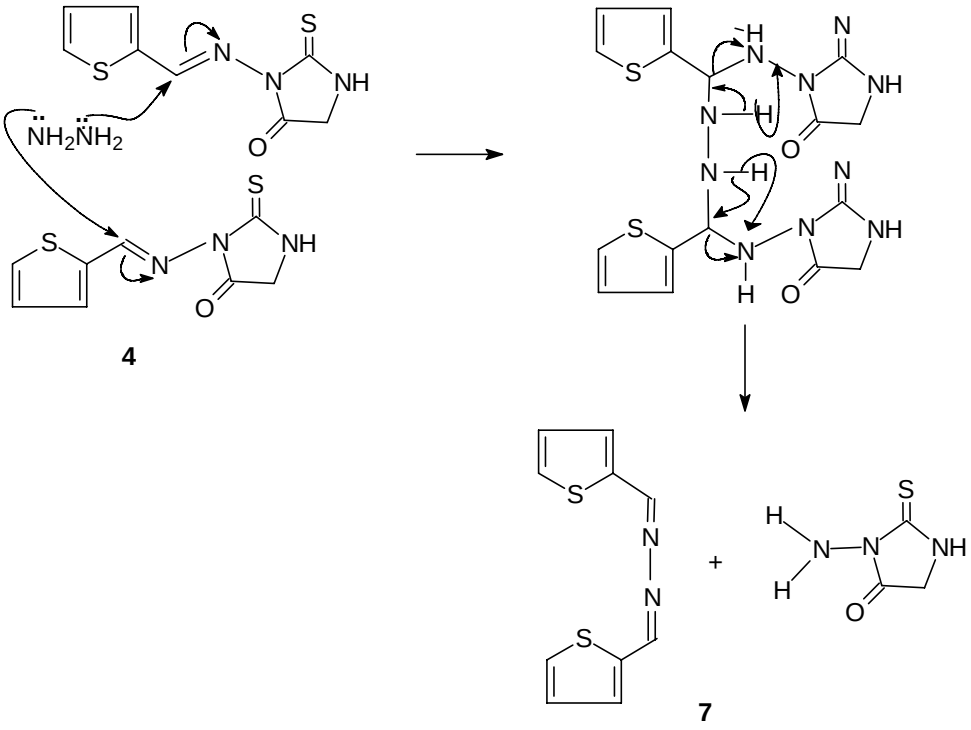
[(thiophen-2-ylmethylene)-amino]-4-oxoimidiazolidin-2-thione **8** (**Scheme III**).

Heating of 3-[(thiophen-2-ylmethylene)-amino]-4-oxo-imidazolidin-2-thione **4** with chloroacetyl chloride to fusion gave the corresponding 1-chloro-methyl-5-thioxo-6-[(thiophen-2-ylmethylene)-amino]-imidazolo [5,1-c]-oxazin-4,7-dione **9**, **(Scheme IV)**. Condensation of **4** with 4-chlorobenzaldehyde in presence of piperidine to fusion led to the formation of 3-[(thiophen-2-yl-methylene)-amino]-4-oxo-5-(4-chloro-benzylidene)-imidazolidin-2-thione **11**. Acylation of **11** with acetic anhydride led to the formation of 1-acetyl-3-[(thiophen-2-yl-methylene)--amino]-4-oxo-5-(4-chlorobenzylidene)-imidazolidin-2-thione **12**. The structure of **12** was also established *via* reaction of compound **10** with 4-chlorobenzaldehyde in presence of piperidine.

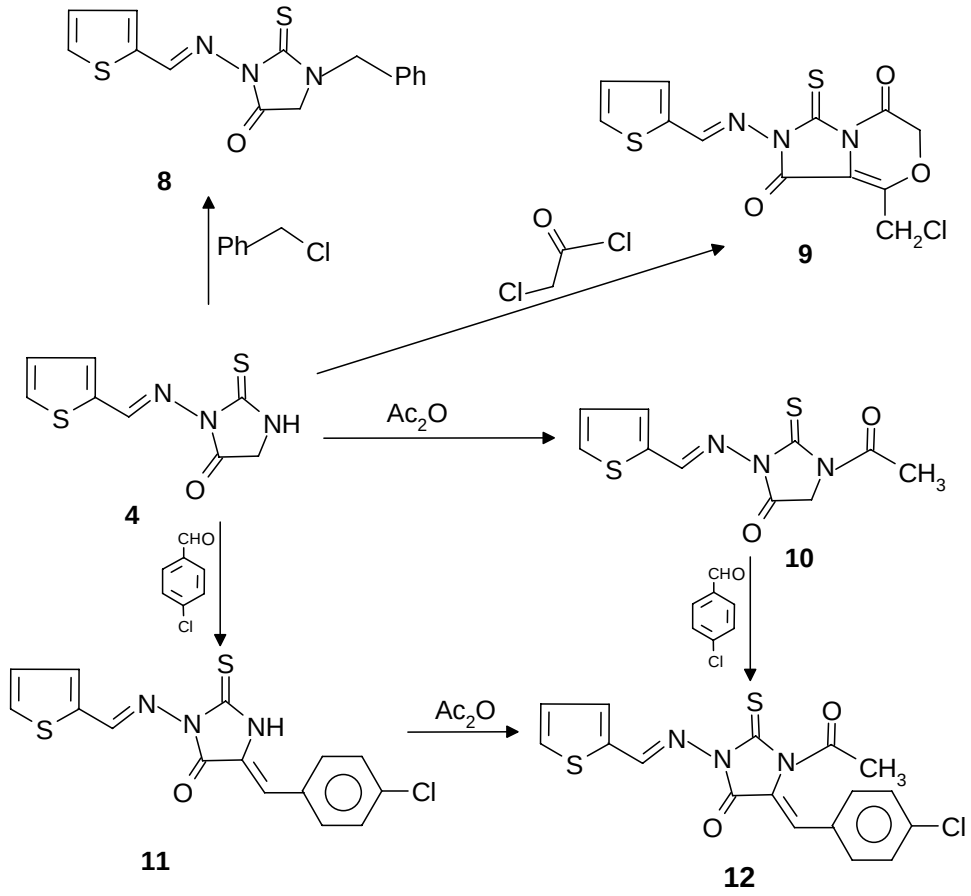
Mass Spectrometery

The mass spectral decomposition modes[10,11] of the prepared heterocyclic compounds containing thiophen ring have been investigated. The mass spectrum of compound **4** showed an intense molecular ion peak at m/z 225 corresponding to the molecular formula $C_8H_7N_3OS_2$. The molecular ion peak was found to be the base peak. The molecular ion of **4** (**Scheme IV**) underwent fragmentation to produce a peak at m/z 180 by losing HCS group. The loss of CH=NH group from the ion with m/z 180 resulted in an ion at m/z 152. The ion at m/z 152 underwent loss of CO and N_2 to give peaks at m/z 124 and 96 respectively.

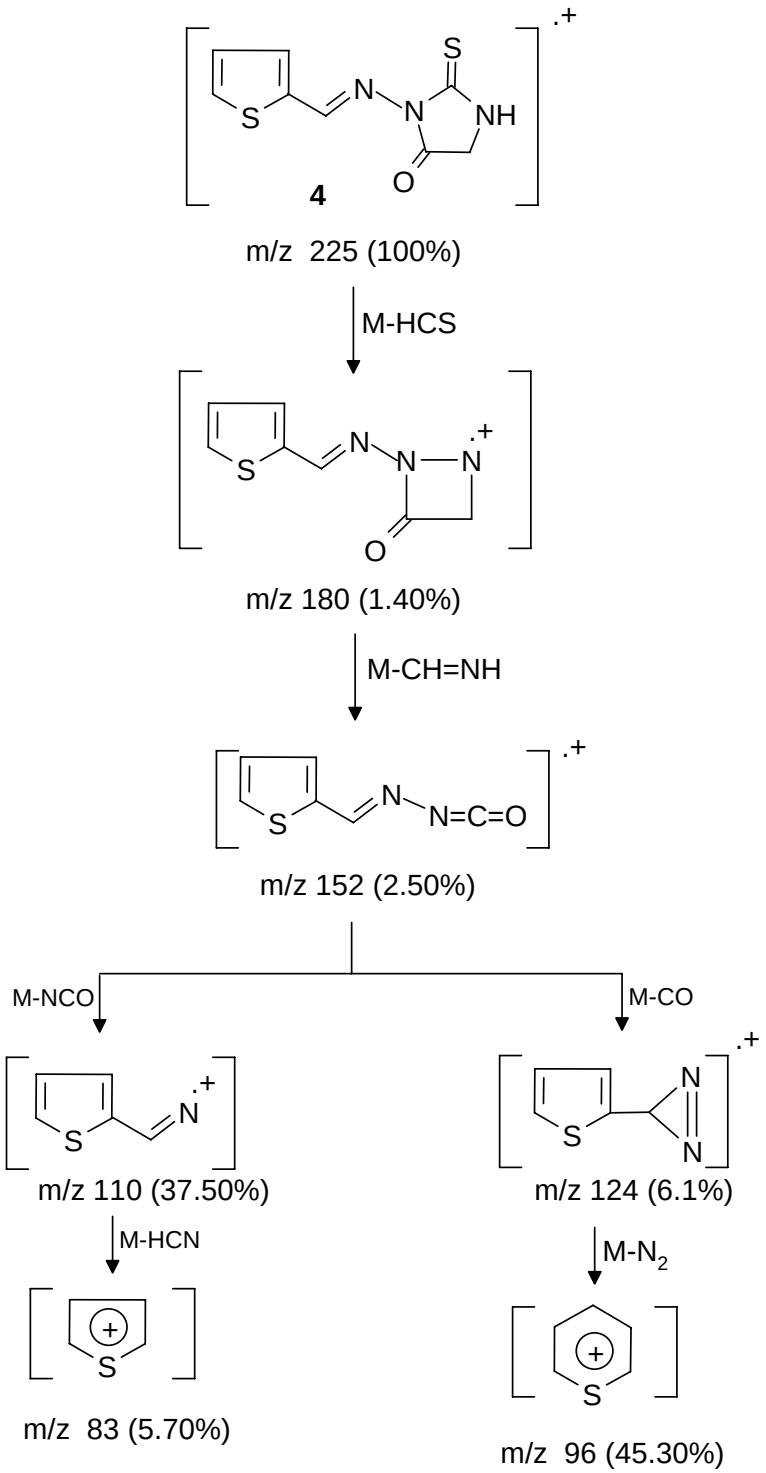
Also the ion at m/z 152 underwent loss of NCO and HCN to give peaks at m/z 110 and 83 respectively, which is a characteristic fragmentation pattern of thiophen-2-ylmethylene amino and thiophen radicals.



Scheme II



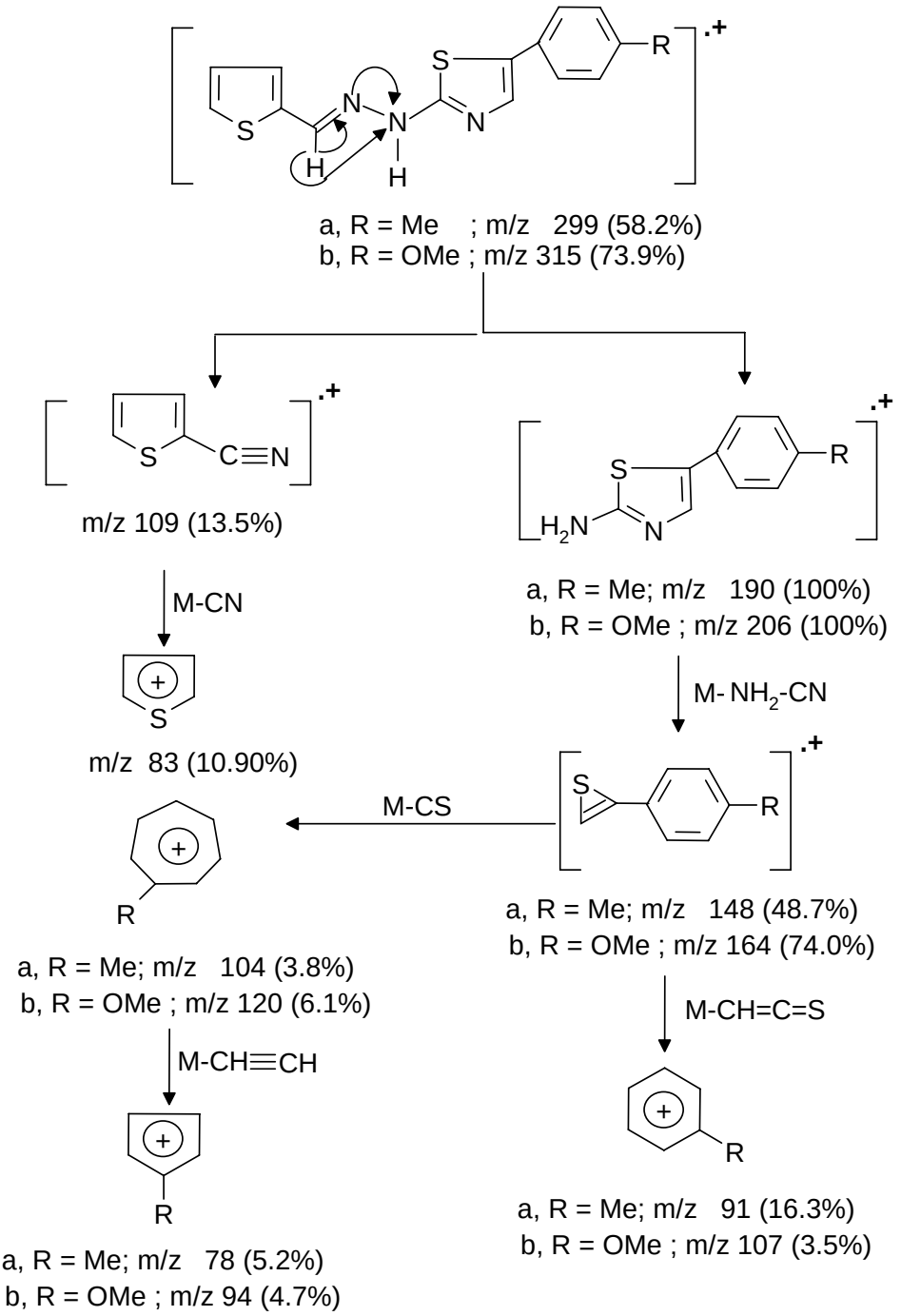
Scheme III



Scheme IV − Mass fragmentation pattern of compound **4**

The mass spectra of compounds **5a,b** are fully consistent with the assigned structures. In most cases, intense molecular ion peaks were observed. Thus, compounds **5a,b** showed intense molecular ion peaks at m/z 299 and 315, consistent with the molecular formulae $C_{15}H_{13}N_3S_2$ and $C_{15}H_{13}N_3OS_2$, respectively.

The molecular ion of compounds **5a** and **5b (Scheme V)** underwent fragmentations to produce peaks at m/z 190 and m/z 206, corresponding to the molecular ion of 5-(4-alkylphenyl)-2-amino-thiazole. It further underwent loss of NH_2CN and CH=C=S to give peaks at m/z 148, 164 and 91, 107 respectively.



Scheme V − Mass fragmentation pattern of compound **5**

Base peaks at m/z 190 and 206, found in the MS of compounds **5a** and **5b**, correspond to the 5-(4-methyl (methoxy) phenyl)-2-amino-thiazole ion. The molecular ions of compounds **5a** and **5b** were also found to undergo fragmentation to produce the ion of 2-cyanothiophen at m/z 109.

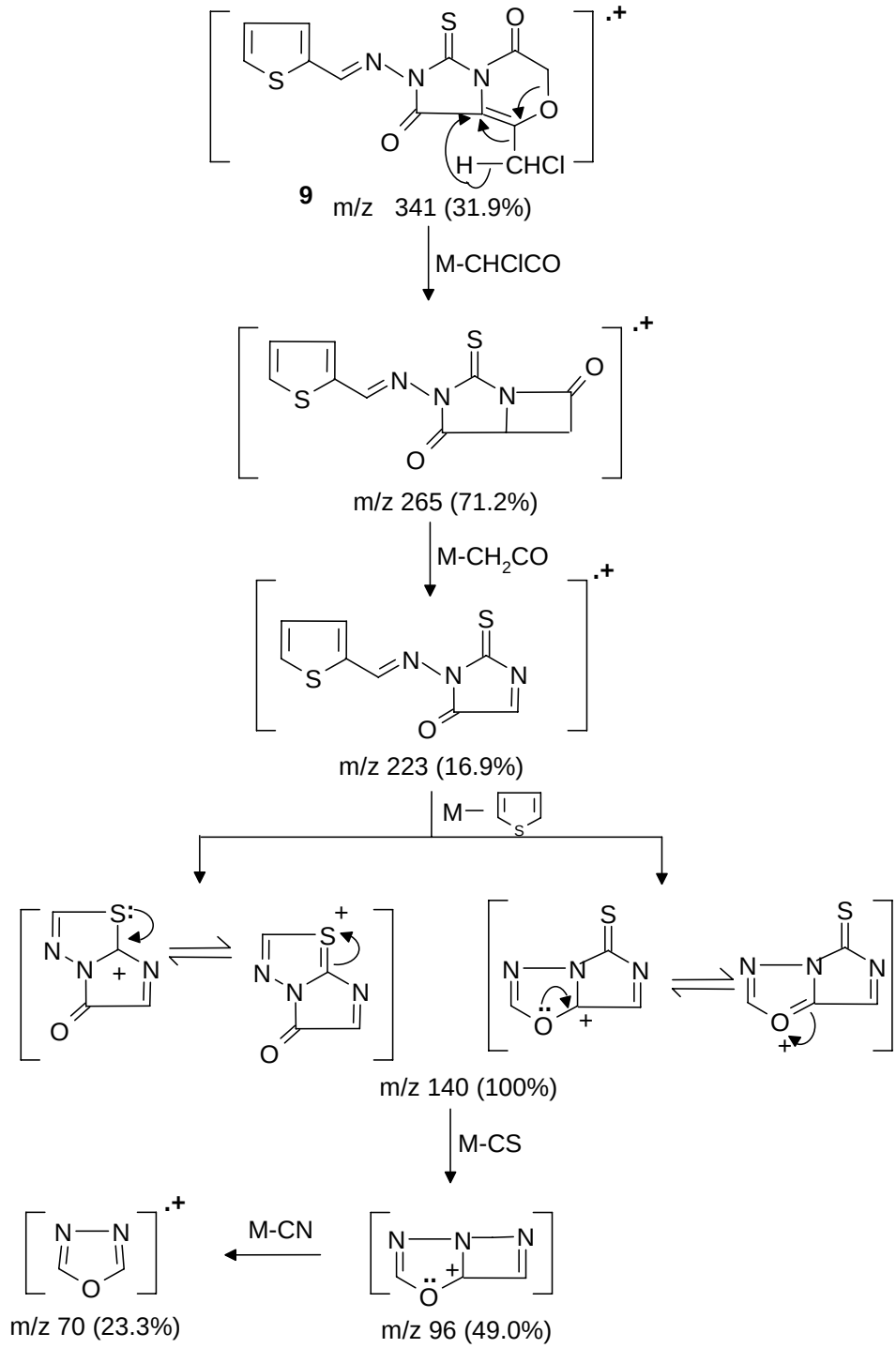
The electron impact ionization mass spectrum of compound **7** shows a base peak (molecular ion) at m/z 220, which further broke to give an ion at m/z 110. The ion of m/z 110 broke to give anion at m/z 96 which lost nitrogen atom. Ion of m/z 96 fragmented to give an ion of m/z 70 which lost an acetylene molecule.

The mass spectrum of compound **9** shows the molecular ion peak at m/z 341, corresponding to the molecular formula $C_{12}H_8N_3ClO_3S_2$. The M+2 peak

was also observed at m/z 343 along with the molecular ion peak due to the presence of isotopes of chlorine atom present in the compound.

The molecular ion of compound **9** underwent fragmentation **(Scheme VI)** to produce the peak at m/z 265 by losing CHClCO. The loss of methylene carbonyl (CH_2CO) from the ion with m/z 265 gave a daughter ion at m/z 223. The common peak at m/z 140 was also observed in this case which is attributed to an ion obtained by the loss of thiophene from the ion of m/z 223. The base ion of m/z 140 underwent loss of CS and CN groups to give peaks at m/z 96 and 70, respectively.

From the mass spectrum of compound **10**, it was concluded that the molecular ion was at m/z 267. The



Scheme VI—Mass fragmentation pattern of compound **9**

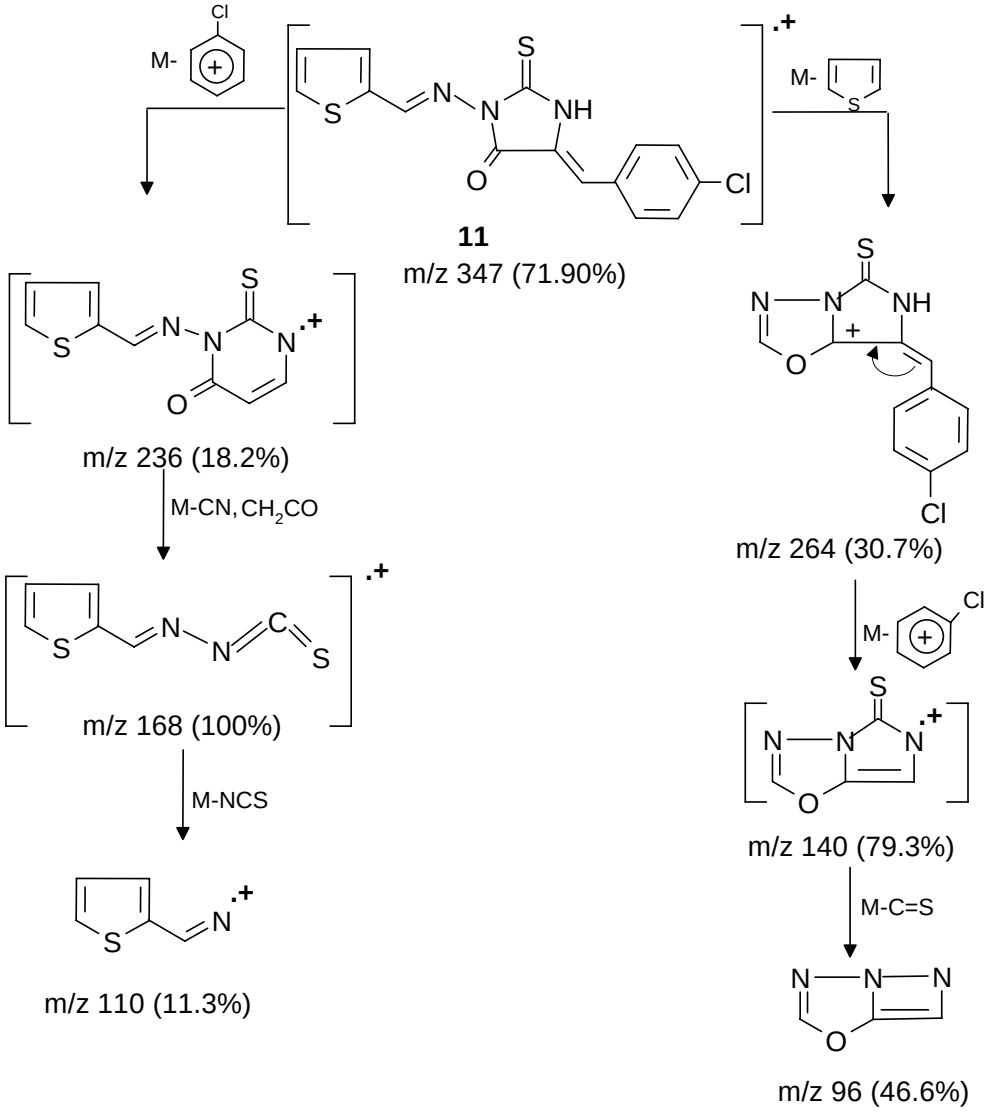
ion of m/z 267 underwent fragmentation to produce a peak at m/z 225 by losing CH_2CO, corresponding to the base peak and the molecular ion of compound **4**. The stable fragment of m/z 225 further broke *via* pathway similar to compound **4** (**Scheme IV**).

The molecular ion peak of compound **11** was observed at m/z 347/349 corresponding to the molecular formula $C_{15}H_{10}ClN_3OS_2$. The loss of *p*-chlorophenyl radical from the molecular ion peak at m/z 347 gave a peak at m/z 236. The common peak at m/z 168 was also observed in this case which is attributed to an ion obtained by the loss of cyano and methylene carbonyl groups from the ion at m/z 236 (**Scheme VII**). The formation of fragment ion at m/z 264 could be explained by the loss of thiophen radical from the molecular ion peak at m/z 347. The loss of *p*-chlorophenylmethylene from the ion at m/z 264 resulted in an ion at m/z 140.

The mass spectrum of compound **12** showed the molecular ion m/z 389/391, corresponding to the molecular formula $C_{17}H_{12}ClN_3O_2S_2$. The loss of methylene carbonyl (CH_2=C=O) from the molecular ion resulted in ion at m/z 347, corresponding to the molecular ion of compound **11**. The fragment ion of m/z 347 which has further broken *via* pathway similar to compound **11**.

Experimental Section

NMR spectra were recorded on a General Electric QE 300 instrument and chemical shifts are given in δ (ppm) with TMS as internal reference. IR spectra were recorded on a Perkin-Elmer 1420 and a Biorad FTS7 spectrometer in KBr pellets. Mass spectra were



Scheme VII—Mass fragmentation pattern of compound **11**

obtained on a Jeol JMS D-300 spectrometer operating at 70eV. Microanalyses were conducted using a 1106 elemental analyzer. Melting points were determined on a Reichet Hot instrument and are uncorrected.

1-(Thiophen-2-ylmethylene)-thiosemicarbaozone, 3. A mixture of **1** (0.01 mole), thiosemicarbazide (0.01 mole) and anhydrous potassium carbonate (0.03 mole) in methanol was heated under reflux for 4hr, then cooled. The reaction mixture was acidified with 1N HCl. The solid formed was filtered, washed with water, dried and purified by recrystallization from benzene to give **3** as colorless crystals. Yield 0.981g; m.p. 170°C; IR(KBr): 3414, 3150 (NH_2), 3234 (NH), 1612 (C=N), 1326 cm^{-1} (C=S). Anal. Found: C, 38.92; H, 3.78; N, 22.70; S, 34.59. $C_6H_7N_3S_2$ requires: C, 38.69; H, 3.58; N, 22-23; S, 34.34%. MS: m/z(%) 186(M^++1, 9.47), 185(M^+, 100), 169(3.41), 168(29.75), 152(4.90), 135 (2.81), 126 (9.87), 125 (24.46), 111 (12, 34), 110(47.54), 109(12.79), 99(18.61), 97 (21.87), 96 (11.87), 84(17.71), 83(16.69), 78 (39.47), 77(15.29), 60(47.78).

3-[(Thiophen-2-ylmethylene)-amino]-4-oxo-imidazolidin-2-thione (4), 5-aryl-2-[(thiophene-2-ylmethylene)-hydrazino]thiazole, 5a, b. A mixture of **3** (0.01 mole), ethyl chloroacetate and ω-bromomethyl aryl ketones (such as 4-methylphenacyl-bromide and 4-methyoxyphenacyl-bromide) (0.01 mole) in ethanol (50 mL) in presence of fused sodium acetate (0.03 mole) was heated under reflux for 6hr, then cooled and poured into water. The resulting solid was filtered off, washed with water, dried and purified by recrystallization from a suitable solvent to give **4** and **5**.

3-[(Thiophen-2-ylmethylene)-amino]-4-oxoimidazolidin-2-thione, 4: Yield 1.755g; m.p. 228°C; IR (KBr): 3348 (NH), 1705 (C=N), 1630 (CH=N), 1311 cm^{-1} (C=S); ^{1}H NMR (DMSO-d_6): δ 3.67 (s, 2H, NCH_2CO), 6.98-7.00 (d, 1H, thiophen), 7.23-7.24(t, 1H, thiophen), 7.33-7.35 (d, 1H, thiophen), 8.38 (s, 1H, CH=N); MS: m/z(%) 226 (M^++1, 12.10), 225 (M^+, 100), 224 (M^+– 1, 5.2), 196 (1.4), 192 (1.20), 152 (2.50), 138 (2.0), 136 (1.20), 111 (29.0), 110 (37.5), 104 (3.7), 96 (45.30), 95 (6.4), 84 (4.20), 83(5.70). 78(10.90), 70 (16.90) 69(7.5), 52 (10.0). Anal. Found: C, 42.48; H, 3.01; N, 18.39; S, 28.17. $C_8H_7N_3OS_2$ requires: C, 42.67; H, 3.11; N, 18.67; S, 28.44%.

5-(4-Methylphenyl)-2-[(thiophen-2-ylmethylene)-hydrazino]-thiazole, 5a: Yield 2.123 g; m.p. 121°C; IR(KBr): 3321 (NH), 1631(C=N), 1605, 1582 cm^{-1} (C=C); ^{1}H NMR (DMSO-d_6): δ 2.25 (s, 3H, CH_3), 6.91-8.1 (m, 8H, thiophen, Ar–H and H–thiazole), 8.41 (s, 1H, CH=N), 10.98 (s, 1H, NH); MS: m/z(%) 300 (M^+ +1, 22.9) (M^+, 58.20), 191 (14.50), 190 (100), 189 (9.70), 148(48.70), 147 (38.80), 146 (4.60), 135(6.60), 134(3.60), 122 (3.20), 121(5.30), 119(3.20), 118(14.30), 111(5.60), 110(18.60), 97(5.80), 96 (13.10), 91 (16.30), 90 (6.00), 84 (5.00), 83 (9.60), 82 (4.60), 78(5.20), 77 (10.80), 70(14.70), 69(13.60), 65 (14.90), 64 (5.80), 52 (13.20). Anal. Found : C, 60.02; H, 4.21; N, 13.98; S, 21.19. $C_{15}H_{13}N_3S_2$ requires : C, 60.20; H, 4.35; N, 14.05; S, 21.40%.

5-(4-methoxyphenyl)-2-[(thiophen-2yl-methylene)hydrazine]thiazole, 5b: Yield 2.330g; m.p. 110°C; IR(KBr): 3315 (NH), 1632(C=N), 1605, 1587 (C=C), 1120, 1010 cm^{-1} (C–O); ^{1}H NMR (DMSO-d_6): δ 3.85 (s, 3H, OCH_3), 6.98 –8.11 (m, 8H, - Ar–H, Thiophen and thiazol ring), 8.41 (s, 1H, CH=N), 10.93 (s, 1H, NH); MS: m/z(%) 316 (M^++1, 18.20), 315 (M^+, 73.90), 314(M^+-1, 4.10), 207 (15.70), 206 (100), 205(13.90), 192(14.50), 191(34.70), 165(8.90), 164(74.00), 163(6.80), 159(14.50), 158(5.40), 149(45.90), 148(5.70), 135(10.50), 134(19.50), 133(14.30), 132(12.30), 122(6.50), 121 (22.60), 120(6.10), 111(15.60), 110(18.70), 109(13.50), 103(10.20), 102(6.00), 97(13.50), 96(21.20), 92(8.70), 91(10.00), 84(6.90), 83(10.90), 82(6.30), 77(27.70), 76(11.10), 70(16.80), 69(20.40) 64(47.20), 63(28.10), 52(14.90), 51(22-10). Anal. Found : C, 57, H, 4.02; N, 13.07; S, 20.12. $C_{15}H_{13}N_3OS_2$ requires: C, 57.14; H, 4.13; N, 13.33; S, 20.32%.

5-Aryl–2–[Thiophen–2–ylmethylen]–acetylhydrazino]thiazole, 6a, b. A solution of **5** (0.01 mole) in acetic anhydride (20 mL) was heated under reflux for 2hr, then cooled and poured into ice-water. The solid obtained was filtered off, washed with water, dried and purified by recrystallization benzene to give **6**.

5-[4–Methylpheyl–2-(thiophen–2–ylmethylene)–1-acetylhydrazino]– thiazole, 6a: Yield 2.285g; m.p. 72ºC; IR (KBr): 1689 (C=O), 1632(C=N), 1610, 1592 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 3H, CH_3), 2.43 (s, 3H, $COCH_3$), 6.97–7.98 (m, 8H, Ar-H and thiophen ring), 8.42 (s, 1H, CH=N); MS: m/z(%) 342(M^+ + 1, 11.30), 341(M^+, 33.51), 299(38.35), 191 (12.30), 190(100), 189(11.30), 148(37.35), 147(27.30), 146(7.20), 135(4.60), 121 (6.20), 118(12.39), 110(21.30), 96(12.61), 91(15.50), 77(12.10), 65(13.90). Anal. Found: C, 59.63, H, 4.27; N, 12.02; S, 18.53 $C_{17}H_{15}N_3OS_2$ requires: C, 59.82; H, 4.40; N, 12.32; S, 18.77%.

5-(4-Methoxyphenyl)–2–[(thiophene–2–ylmethylene)-1-acetylhydrazino]thiazole, 6b: Yield 2.463g; m.p. 76ºC; IR(KBr): 1692 (C=O), 1630(C=N), 1613, 1583(C=C), 1130, 1010 cm^{-1} (C-O); ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3H, $COCH_3$), 3.98(s, 3H, OCH_3), 6.99-7.99 (m, 8H, Ar-H and thiophen ring), 8.42 (S, 1H, CH=N); MS: m/z(%) 358 (M^+ + 1, 11.20), 357 (M^+, 27.30), 315(61.30), 206(100), 192(13.30), 191(27.30), 165(11.30), 164(63.91), 159(12.30), 149(35.31), 135(9.71), 134(14.20), 121(18.60), 110(23-20), 109(12.30). Anal. Found : C, 57.02; H, 4.01; N, 11.49; S, 17.73. $C_{17}H_{15}N_3O_2S_2$ requires: C, 57.14; H, 4.20; N, 11.76; S, 17.93%.

1, 2–Bis-(thiophen–2–ylmethylene) – hydrazone, 7: A solution of **4** or **5** (0.01 mole) and hydrazine hydrate (0.02 mole) in ethanol (50 mL) was heated under reflux for 2hr, then cooled and acidified with dilute HCl (2%). The crude product obtained was filtered, washed with water, dried and purified by recrystallization from benzene to give **7** as yellow crystals. Yield 0.946g; m.p. 138ºC; IR(KBr): 3095 (CH olefinic), 1630 cm^{-1} (C=N); ^{1}H NMR (DMSO–d_6): δ 7.20 – 7.82 (m, 6H, thiophene ring), 8.92 (s, 2H, 2×CH=N); MS : m/z(%) 221 (M^++1, 13.20), 220(M^+, 100), 193(15.30), 192(30.00), 191(14.60), 148(3.00), 147(13.40), 111(4.70), 110(31.70), 109(5.40), 97(4.00), 96(16.00), 95(9.40), 84(8.10), 83(11.5), 82(3.00)70(17.60), 69(11.90), 63(4.70), 52(11.00), 51(5.70). Anal. Found: C, 54.45; H, 3.49; N, 12.57; S, 28.89. $C_{10}H_8N_2S_2$ requires: C, 54.55; H, 3.64; N, 12.73; S, 29.10%.

1-Benzyl–3–[(thiphen–2–ylmethylene)–amino]–4–oxo-imidiazolidin–2–thione, 8. A mixture of **4** (0.01mole) and benzyl chloride (0.01 mole) in DMF (25mL) was heated under reflux for 4hr, then cooled and poured into water. The resulting product was filtered, washed with water, dried and purified by recrystallization from ethanol to give **8** as pale yellow crystals. Yield 1.985g; m.p. 180ºC; IR(KBr): 1701 (C=O), 1631(C=N), 1616, 1595(C=C), 1319cm^{-1} (C=S); MS: m/z(%) 315 (M^+, 6.60), 225(43.40), 199(11, 40), 193(12.30), 154(5.20), 148(4.60), 136(3.70), 128(4.50), 127(6.90), 111(27.40), 110(35.40), 109(7.70), 105(5.20), 104(10.30), 97(13.00), 96(100.0), 95(25.90), 92(8.40), 91(95.50), 90(18.60), 84(8.80), 83(12.30), 82(8.7), 78(7.30), 77(16.30), 70(63.00), 69(34.60), 65(39.80), 64(11.30), 63(29.40), 62(15.50), 52(23.60), 51(43.70). Anal. Found: C, 57.00; H, 4.02; N, 13.03; S, 20.11. $C_{15}H_{13}N_3OS_2$ requires: C, 57.14; H, 4.13; N, 13.33; s, 20.32%.

1-Chloromethyl-5-thioxo-6-[(thiophen-2-ylmethylene)amino]imidazolo[5, 1-c]oxazin-4, 7-dione, 9: A mixture of **4** (0.01 mole) and chlorocetyl chloride (0.03 mole) was fused on a hot plate for 15-20 min. The reaction mixture was added to boiling benzene (50mL) and heated under reflux for 2hr, then cooled. The solid formed was filtered off, washed with benzene, dried and purified by recrystallization from methanol to give **9** as yellow crystals. Yield 2.148g; m.p. 220ºC; IR (KBr): 1715, 1705(C=O), 1630(C=N), 1613, 1583(C=C), 1315(C=S), 1130 1100, 1050cm^{-1} (C-O); ^{1}H NMR (DMSO-d_6): δ 4.20 (s, 2H, CH_2Cl), 4.81(s, 2H, OCH_2CO), 7.28–8.01 (m, 3H, thiophen ring), 8.55 (s, 1H, CH=N); MS: m/z(%) 343 (M^++2, 22.80), 341(M^+, 31.90), 267(10.70), 266(47.00), 265(71.20), 237(5.60), 236(16.60), 223(16.90), 168(5.80), 167(5.30), 142(15.30), 141(21.50). 140(100), 139(16.00), 110(4.00). 109(4.00), 108(33.50), 97(12.80), 96(49.00), 95(20.80). 84(13.10), 83(1.50), 82(23.00), 79(19.50), 77(56.80), 72(49.40), 71(10.70), 70(23.50), 69(37.20), 63(23.9), 58(23.30), 51(38.60), 50(21.90). Anal. Found: C, 42.01; H, 2.21; N, 12.08; Cl, 10.16; S, 18.50. $C_{12}H_8N_3ClO_3S_2$ requires: C, 42.23; H, 2.35; N, 12.32; Cl, 10.41; S, 18.77%.

1-Acetyl–3-[(thiophen–2–ylmethylene)–amino]-4-oxo-imidzolidin-2-thione, 10: A solution of **4** (0.01mole) in acetic anhydride (25mL) was heated under reflux for 2hr, then cooled and poured onto ice-water. The resulting product was filtered off, washed with water, dried and purified by recrystallization from benzene to give **10** as pale yellow crystals. Yield 1.896g; m.p. 170ºC; IR(KBr): 1735, 1661 (C=O), 1625 (C=N), 1608, 1595 (C=C), 1315 cm^{-1} (C=S); ^{1}H NMR (DMSO-d_6): δ 2.11 (s, 3H, $COCH_3$), 3.65 (s, 2H, NCH_2CO), 6.99 - 7.01 (d, 1H, thiophen), 7.24 - 7.26 (t, 1H, thiophen), 7.71 - 7.74 (d, 1H, thiophen), 8.41 (s, 1H, CH=N); MS: m/z(%) 268 (M^++1, 5.60), 267(34.80), 226(14.00), 225(100), 224 (8.90), 197(1.30), 196(5.50), 155(3.90), 154(21.40), 152(3.90), 128(7.20), 127(14.70), 123(6.60), 122(13.80), 116(19.80), 111(30.50), 110(47.10), 109(13.00), 97(12.10), 96(43.50), 84(6.60), 83(5.20), 70(16.20), 69(14.70), 58(12.10). Anal. Found : C, 44.59; H, 3.21; N, 15.52; S, 23.67. $C_{10}H_9N_3O_2S_2$ requires : C, 44.94; H, 3.37; N, 15.73; S, 23.97%.

3-[(Thiophen-2-ylmethylene)-amino]-4-oxo-5-(4-chlorobenzylidene)-imidazolidin-2-thione, 11. A mixture of **4** (0.01mole), 4-chlorobenzaldehyde (0.01mole) and piperidine (1mL) was fused on a hot plate at 120-125ºC for 1 hr. The reaction mixture was

cooled and acidified with dilute HCl (2N). The crude product was filtered off, washed with water, dried and purified by recrystallization from ethanol to give **11** as yellow crystals. Yield 2.637g; m.p. 248ºC; IR(KBr): 3251 (NH), 1708 (C=O), 1630 (C=N), 1605, 1596 (C=C), 1311 (C=S) cm^{-1}; ^1H NMR (DMSO-d_6): δ 6.98-8.01(m, 7H, Ar - H and thiophen ring), 8.49 (s, 1H, CH=N), 11.03 (s, 1H, NH); MS: m/z(%) 349(M^++2, 40.0) 347(M^+, 71.90), 346(M^+-1, 16.10), 321 (7.30), 319 (24.70), 266 (11.8), 264 (30.70), 238 (5.60), 236 (18.20), 226 (2.5), 224 (7.00), 197 (9.90), 196 (5.10), 195 (5.10), 170 (36.90), 169 (29.30), 168 (100.0), 142 (10.10), 141 (13.20), 140 (79.30), 138 (14.10), 136 (9.90), 135 (3.30), 134 (9.50), 133 (27.50), 126 (8.40), 125 (7.40), 124 (24.30), 111 (17.30), 110 (11.30), 109 (2.80), 96 (46.60), 95 (9.30), 90 (6.10), 89 (60.30), 76 (3.70), 75 (18.30), 63 (20.50), 62 (7.80), 51 (11.60), 50 (12.20). Anal. Found: C, 51.61; H, 2.54; N, 12.00; Cl, 10.01; S, 18.21. $C_{15}H_{10}N_3ClOS_2$ requires: C, 51.87; H, 2.88; N, 12.10; Cl, 10.23; S, 18.44%.

1-Acetyl-3-3[(thiophen-2-ylmethylene)-amino]-4-oxo-5-(4-chlorobenzylidene)-imidazoliodin-2-thione, 12. A solution of **11** (0.01 mole) in acetic anhydride (25mL) was heated under reflux for 2hr, then cooled and poured into ice-water. The resulting product was filtered, washed with water, dried and purified by recrystallization from benzene to give **12** as yellow crystals. Yield 2.956g; m.p. 165°C, IR (KBr): 1705 (CO), 1623 (C=N)1610, 1580 (C=C), 1315 cm^{-1} (C=S); ^1H NMR (DMSO-d_6): δ 2.12 (s, 3H, $COCH_3$), 6.99-8.01 (m, 7H, Ar-H and thiophen ring), 8.46 (s, 1H, CH=N); MS: m/z (%) 391 (M+2, 10.50), 389 (M^+, 20.60), 349 (14.20), 348 (12.1), 347 (28.30), 320 (3.6), 319 (17.70), 266 (2.80), 265 (1.20), 264 (7.10), 238 (4.10), 237 (3.10), 236 (20.10), 197 (3.60), 196 (6.70), 195 (3.10), 182 (13.10), 181 (4.60), 170 (12.30), 169 (14.40), 168 (33.50), 155 (12.50), 154 (7.90), 141 (15.30), 140 (100), 137 (6.10), 136 (10.50), 124 (8.70), 123 (6.10), 109 (3.70), 108 (13.70), 96 (37.50), 95 (14.50), 90 (4.40), 89 (26.00), 77 (10.0), 75 (17.30), 70 (11.8), 69 (22.20), 63 (22.5). Anal. Found: C, 52.23; H, 2.98; N, 10.52; Cl, 9.01; S, 16.33. $C_{17}H_{12}ClN_3O_2S_2$ requires: C, 52.44; H, 3.08; N, 10.80; Cl, 9.13; S, 16.45%.

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