SYNTHESIS AND REACTIONS OF 4*H*-IMIDAZO[4, 5-*e*][2, 1, 3]BENZOTHIADIAZOL-5(6*H*)-ONE

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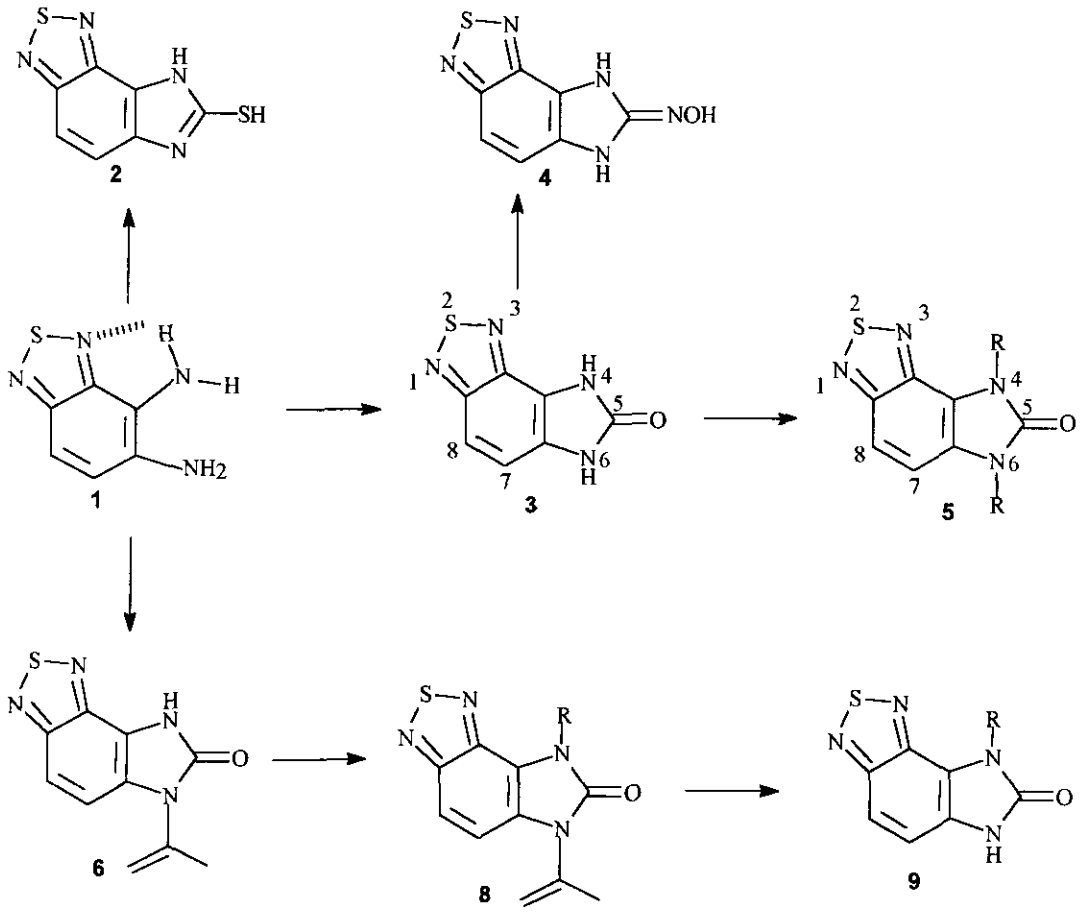
Abstract - 4*H*-Imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one (**3**) has been prepared by the condensation of 4,5-diamino-2,1,3-benzothiadizole (**1**) with urea. 4,5-Diamino-2,1,3-benzothiadizole (**1**) was also fused with thiourea to get the 5-mercapto-4*H*-imidazo [4,5-*e*][2,1,3]benzothiadiazole (**2**). Reactions on the compound (**3**) have been investigated.

Benzothiadiazoles have been broadly used in the areas of pharmaceutical and agricultural applications.[1] Several of them are reported to be the excellent insecticide synergists.[2] A few derivatives have got sedative and hypnotic actions comparable to those of benzodiazepines.[3] A good number of imidazobenzothiadiazoles have been patented as insecticides, herbicides[4] and fungicides.[5] Many imidazolone derivatives are widely used as drugs.[6] Chlorimpiphenine(neuroleptic), domperidone(antiemetic), mephenytoin(anticonvulsant) niridazole(antischistosomal) etc. are some of the drugs which contain imidazolone moiety besides a heterocyclic unit. We now wish to report the synthesis and a few chemical properties of 4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one.

The title compound (**3**) has been prepared by the direct fusion of 4,5-diamino-2,1,3-benzothiadiazole (**1**) with urea. 5-Mercapto-4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazole (**2**), an analogue of **3** has been produced when the diamine (**1**) has been fused with thiourea. The synthesis of the compound (**2**) has already been reported by us[7] in a different route. Though the yield in this method is lower than that of the carbon disulphide method, it may be considered to be the better one due to the shorter reaction times, easy work up and cheaper chemicals (Scheme 1). The structure of **3** has been confirmed by its elemental, ir, ^{1}H nmr and mass spectral data. The ir absorption band

between 3138-3000 cm^{-1} has been assigned to the intermolecularly hydrogen bonded N-H stretching vibrations. A strong absorption band at 1750-1736 cm^{-1} reveals the presence of a keto group.

Scheme 1



The ^1H nmr spectrum of **3** supported the assigned structure. The NH protons appeared as a broad singlet at δ 11.1. Another broad singlet appeared at δ 11.9-12.0 may be assigned to OH group due to the tautomerism. The protons at C-7 and C-8 positions appeared as doublets centered at δ 7.5 and δ 7.8 respectively. The molecular ion peak appeared as the base peak in the mass spectrum of **3** along with its attendant M+2 peak due to the sulphur. The molecular ion ejected CO to give another abundant peak at *m/z* 164. The other prominent peaks recorded are present at *m/z* 149 (M- HNCO), 136 (164-S).

The reaction of 4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one (**3**) with various alkyl and aralkyl halides in a

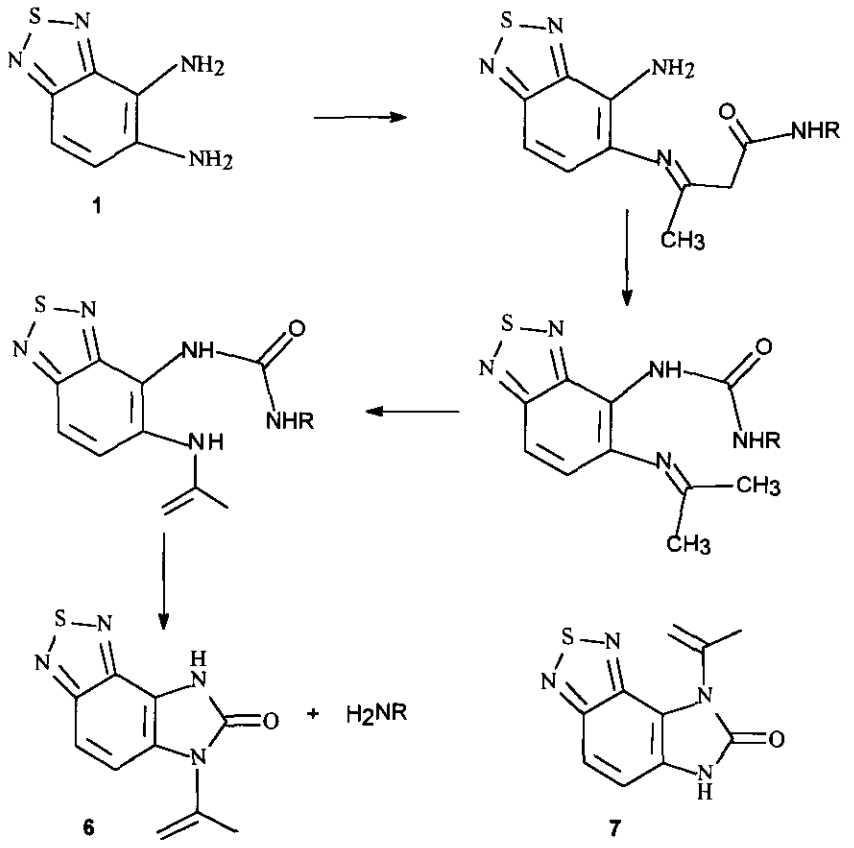
solvent like methanol or ethanol containing inorganic base gave 4,6-disubstituted derivatives (**5**). The structures of these compounds have been confirmed by their elemental and spectral data

The ir spectra of the disubstituted derivatives (**5**) possessed an absorption band at 1750-1685 cm^{-1} due to the presence of an oxo group at C-5 carbon. The absence of NH absorptions in these compounds as compared to the compound (**3**) confirmed the structures assigned for compounds (**5**). The chemical shifts in ^1H nmr spectra of these compounds indicated the presence of aromatic protons which appeared at δ 7.45 - 7.8. The ^1H nmr spectrum of **5a** displayed two singlets for the two methyl groups present on nitrogen atoms. A singlet at low field region i.e. at δ 4.0 may be assigned to the methyl group present at 4 position. This is due to the anisotropy of C=N present in the thiadiazole ring. The remaining methyl group appeared as a singlet at high field region i.e. at δ 3.6. This pattern was also observed in all the dialkyl / diaralkyl derivatives of **3**. The characteristic peaks for other protons in the side chain were also present. The mass spectra of dialkyl / diaralkyl derivatives of **3** indicated similar type of fragmentation to that of **3**. In majority of the cases, the molecular ion was recorded as the base peak.

The 4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one (**3**) could not be condensed with primary amines and hydrazine hydrate. But the condensation was possible with hydroxylamine hydrochloride in ethanol in presence of sodium hydroxide to give a compound (**4**) in a very low yield. The repeated recrystallisation in different solvents also did not give pure compound. But the structure can be confirmed convincingly by its mass spectrum. [Ms (*m/z*); 208(MH^+, 7), 207(M^+, 10), 205(M-2, 7%), 193(MH^+ -NH_2, 100), 189(M-H_2O), 175(M-S), 164 (M-HNCO, 40)]. The diamine (**1**) has been fused with thiourea to get 5-mercapto-4*H*-imidazo[4,5-*e*][2,1,3]-benzothiadiazole (**2**). The melting point and its spectral characteristics have matched with those of an authentic sample reported by us[7] earlier. The 6-isopropenyl-4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one (**6**) has been synthesised according to a reported method.[8] The formation of this compound can be explained by the following scheme which is based on the reactions [9] of methyl acetoacetate and orthophenylenediamine (Scheme 2). Initial condensation of two moles of the diamine with one mole of methyl acetoacetate in toluene or xylene has led to the formation of final compound (**6**). The formation of the compound (**7**), an isomer of **6** has not been observed. This may be partly due to the steric hinderance offered by the thiadiazole ring which blocks the approach of methyl acetoacetate towards amino group at the 4th position of diamine (**1**), and partly due to the presence of hydrogen

bonding (Scheme1). Formation of **6** has also been confirmed by the following series of reactions. Isopropenylimidazobenzothiadiazole (**6**) has been alkylated with *p*-bromophenacyl bromide at the 4 position of **6** in presence of a base to give **8b**. On comparing the ^{1}H nmr spectrum of this compound with that of its corresponding disubstituted derivative (**5h**) it has been found that the methylene singlet which appeared at δ 5.5 in the compound (**5h**) is absent in the ^{1}Hnmr spectrum of **8b**, whereas the second methylene singlet at δ 5.9 in the ^{1}Hnmr spectrum of **5h** has matched with the methylene singlet appeared at δ 6.1 in the ^{1}Hnmr spectrum of **8b**. The small shift in the absorption position may be due to a change in the pmr solvent system. The compound (**8b**) has been hydrolysed by heating with conc. hydrochloric acid to get **9b**. The above series of reactions and the corresponding pmr data confirm the assigned structures of the compounds (**6**, **8** and **9**) (Scheme 1).

Scheme 2



H_2NR = Diamine, **1**

CONCLUSION: We can conclude that the compound (**6**) is formed from **1** as expected from physical organicchemistry principles. Compounds (**2**) and (**3**) may serve as intermediates in the organic synthesis.

EXPERIMENTAL

The melting points were determined in open capillaries and are uncorrected. The ir spectra were recorded on Shimadzu FT IR - 8101M instrument. The ^{1}H nmr spetra were scanned on Varian Gemini FT NMR instrument at 200 MHz using TMS as the internal reference in δ ppm. The mass spetra were obtained from HP MS EM-5989A at 70 ev.

1. Preparationof4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one(**3**).

4,5-Diamino-2,1,3-benzothiadiazole (**1**, 10.5 g, 0.63 mol) and urea (21.0 g, 0.35 mol) were fused and maintained at 160-165^{O}C for 3 h with vigorous stirring. Then the reaction mixture was cooled to ambient temperature. The residue that separated was purified by refluxing in 100 ml of 10% sodium hydroxide solution containing 5.0 g of activated charcoal followed by filtration. The filtrate was cooled to ambient temperature and was acidified with acetic acid to get the compound. Yield, 10.5 g (87%); mp >340^{0}C. The above compound was also obtained in benzene and xylene, but the yield was low in benzene. Anal. Calcd for $C_7H_4N_4OS$: C, 43.75; H, 2.08; N, 29.17; S, 16.67. Found: C, 43.70; H, 2.07; N, 29.15; S, 16.65. Ir (cm^{-1}): 3138-3000, 1750-1736. ^{1}H Nmr (DMSO-d_6, δ ppm): 11.1 (1H, br s, NH), 11.9 - 12.0 (1H, br s, OH), 7.8 (1H, d, J = 10 Hz, C-8), 7.5 (1H, d, J = 10 Hz, C-7). Ms (*m/z*) : 194 ((M+2, 9), 193 (M+1, 40), 192 (M$^+$, 100), 164 (M - CO, 26), 149 (M-HNCO, 5), 136 (164-S, 6).

2. Preparation of 5-Mercapto-*4H*-imidazo[4,5-*e*][2,1,3]benzothiadiazole (**2**).

The procedure utilised for preparing compound (**3**) was adopted to prepare this compound. The diamine (**1**, 10.5 g, 0.063 mol) and thiourea (2.48 g, 0.315 mol) gave the compound (**2**). It was purified by refluxing in 100 ml of 10% sodium hydroxide solution containing a small quantity of activated charcoal followed by filtration. The filtrate was cooled to ambient temperature and was acidified with acetic acid to get the compound. Yield,7.0 g (53%); mp 280-283^{O}C (mp 278^{O}C) [7].

3. Preparation of Oxime (**4**).

The compound (**3**)(9.6 g, 0.05 mol) was dissolved in ethanol (50 ml) containing sodium hydroxide (4.0 g, 0.1 mol) and water (10 ml) and refluxed for 1/2 h. The hydroxylamine hydrochloride (3.5 g, 0.05 mol) was slowly added to

the reaction mixture and it was allowed to reflux for 8 h. The reaction mixture was cooled and poured into ice-cold water(200 ml) containing conc. hydrochloric acid(10 ml). The reaction mass was kept at 10°C for 0.5 h and filtered to collect the precipitate. The precipitate was washed with water and dried. It was recrystallised from dimethyl sulphoxide. Yield, 4.0 g (19 %); mp 330° C (decomp.). Ir(cm^{-1}): 3300-3000 (br, N-H, O-H), 1651, 1575, 1399, 1055. ^{1}H Nmr (DMSO-d_6 , δ ppm): 7.6-7.8 (2H, Ar), 11.1 (2H, br), 11.9 (1H, br). Ms(*m/z*); 208 (MH^+, 7), 207 (M^+ , 10), 205 (M-2, 7%), 193 (MH^+ -NH_2, 100) 189 (M-H_2O). 175 (M-S), 164 (M-HNCO, 40).

4. Preparation of 4,6-Disubstituted 4*H*-Imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-ones (**5a-j**).

General procedure: 4*H*-Imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one(**3**, 1.92 g, 0.01 mol) was dissolved in methanol (50 ml) containing water (10 ml) and sodium hydroxide (0.8 g, 0.02 mol). Alkyl / aralkyl halide (0.02 mol) was charged slowly to the above refluxing solution. Reaction took 8 h of heating for completion. A solid was separated when the reaction mass was cooled to ambient temperature which was collected by filtration. The precipitate was washed with 10% sodium hydroxide solution to remove the unreacted compoud (**3**) and then with water. The solid thus obtained was dried. The compounds **5a-e** were purified from aq. dimethyl sulfoxide and **5f-j** were purified from aq. dioxan. **5a**: R = CH_3 . Yield, 76%; mp 212-214°C. Anal. Calcd for $C_9H_8N_4OS$; C, 49.09; H, 3.63; N, 25.45; S, 14.54. Found: C, 49.11; H, 3.64; N, 25.43; S, 14.50. Ir(cm^{-1}): 1710-1696 (br, C=O), 1609, 1560. ^{1}H Nmr ($CDCl_3$, δ ppm): 7.8 (1H, d, J=10 Hz, C-8), 7.5 (1H, d, J=10 Hz, C-7), 4.0 (3H, s, CH_3 at 4th position) 3.6 (3H, s, CH_3 at 6th position). Ms(m/z): 222 (M+2, 8) 221 (M+1, 41), 220 ,(M+, 100), 205 (M-CH_3, 10), 191 (M-CHO, 17), 177 (205-CO, 26) 150 (177-HCO, 16). **5b**: R=C_2H_5 . Yield, 73%; mp 200-202°C. Anal. Calcd for $C_{11}H_{12}N_4OS$; C, 53.22; H, 4.83; N, 22.58; S, 12.90. Found: C, 53.20; H, 4.84; N, 22.56; S, 12.93. Ir(cm^{-1}): 1725-1705(C=O), 1610, 1580. ^{1}H Nmr ($CDCl_3$, δ ppm): 7.90 (1H, d, J=9 Hz, C-8), 7.6 (1H, d, J=9 Hz, C-7), 4.3 (2H, q, J=6 Hz, CH_2 at 4th position), 3.9 (2H, q, J=6 Hz, CH_2 at 6th position), 1.2-1.0 (6H, t, J=6 Hz, CH_3). Ms(m/z): 250 (M+2, 12), 248 (M^+, 100), 233 (M-CH_3, 33), 219 (M-C_2H_5, 61), 205 (233-C_2H_4, 67). **5c**: R=C_3H_7 . Yield, 62%; mp 194-196°C. Anal. Calcd for $C_{13}H_{16}N_4OS$; C, 56.52; H, 5.79; N, 20.29; S, 11.59. Found: C, 56.50; H, 5.81; N, 20.27; S, 11.57. Ir(cm^{-1}): 1755 (br, C=O), 1672, 1576. ^{1}H Nmr($CDCl_3$, δ ppm): 7.75 (1H, d, J=8 Hz, C-8), 7.5 (1H, d, J=8 Hz, C-7), 4.4 (2H, t, J=6 Hz, CH_2 at 4th position), 4.0 (2H, t, J=6 Hz, CH_2 at 6th position), 1.75-2.0 (4H, m, J=6 Hz, central CH_2 groups in side chain), 0.95-1.5 (6H, t, J=6 Hz, CH_3 groups). Ms(m/z): 278 (M+2, 15), 277 (M+1, 71), 276 (M+, 100), 247 (M-C_2H_5, 25), 234 (M-C_3H_7, 52), 205 (234-C_2H_5,

25), 177 (205-CO, 24). **5d**: R=CH_2-CH=CH_2 . Yield, 36%; mp 188-190°C. Anal. Calcd for $C_{13}H_{12}N_4OS$; C, 57.35; H, 4.41; N, 20.59; S, 11.76. Found: C, 57.33; H, 4.40; N, 20.60; S, 11.71. Ir(cm^{-1}): 1715, 1615, 1600. ^{1}H Nmr($CDCl_3$, δ ppm): 7.80 (1H, d, J=8 Hz, C-8), 7.5 (1H, d, J=8 Hz, C-7), 4.5 (2H, d, J=6 Hz, CH_2 at 4th position), 4.1 (2H, d, J=6 Hz, CH_2 at 6th position), 5.1-4.8 (6H, m, CH=CH_2). Ms(m/z): 272 (M^+ , 100), 246 (M-C_2H_2 , 43), 220 (246-C_2H_2 ,48), 205 (220-CH_3 , 72). **5e**: R=CH_2 -CH-CH_2(O) (epoxide). Yield, 42%; mp 186-188°C. Anal. Calcd for $C_{13}H_{12}N_4O_3S$; C, 51.31; H, 3.95; N, 18.42; S, 10.52. Found: C, 51.29; H, 3.92; N, 18.40; S, 10.49. Ir(cm^{-1}): 1720-1705, 1617, 1559. ^{1}H Nmr(DMSO-d_6 , δ ppm): 8.0 (1H, d, J=8 Hz, C-8), 7.6 (1H, d, J=8 Hz, C-7), 4.6-4.2 (10H, m, aliphatic H). Ms(m/z): 304 (M^+ , 12), 271 (M-SH), 261 (M-C_2H_3O, 5), 241 (271-CH_2, O, 30), 213 (241-CO, 13), 205 (261-C_3H_4 O, 12). **5f**:: R=CH_2-CO-C_6H_5 . Yield, 47%; mp 221-222°C. Anal. Calcd for $C_{23}H_{16}N_4O_3S$; C, 64.48; H, 3.74; N, 13.08; S, 7.47. Found: C, 64.46; H, 3.75; N, 13.10; S, 7.43. Ir(cm^{-1}): 1714-1695 (br, C=O), 1591, 1560. ^{1}H Nmr(DMSO-d_6, δ ppm): 8.1 (4H, m, ortho to C=O), 7.75-8.0 (6H, m, Ar-H), 6.05 (2H, s, CH_2 at 4th position), 5.8 (2H, s, CH_2 at 6th position). Ms(m/z): 430 (M+2, 8), 428 (M^+ , 42), 323 (M-COC_6H_5, 25), 295 (323-CO, 10), 218 (323-COC_6H_5, 13), 105 (C_6H_5CO, 100). **5g**: R=$CH_2COC_6H_4Cl(p)$. Yield, 58%; mp 232-235°C. Anal. Calcd for $C_{23}H_{14}N_4O_3Cl_2S$; C, 55.53; H, 2.82; N, 11.27; Cl, 14.28, S, 6.43. Found: C, 55.54; H, 2.81; N, 11.25; Cl, 14.25, S, 6.40. Ir(cm^{-1}): 1714-1697 (br, C=O) 1591, 1560. ^{1}H Nmr ($CDCl_3$, δ ppm): 8.1 (4H, m, ortho to C=O), 7.8 (1H, d, J=10 Hz, C-8), 7.55 (4H, m, ortho to Cl), 7.35 (1H, d, J=10 Hz, C-7), 5.9 (2H, s, CH_2 at 4th position), 5.5 (2H, s, CH_2 at 6th position). Ms(m/z): 496 (M+., 67), 498 (M+2, 51), 357 (M-COC_6H_4,38), 313 (13), 278 (24). **5h**: R=$CH_2COC_6H_4Br(p)$. Yield, 69%; mp 230-232°C. Anal. Calcd for $C_{23}H_{14}N_4O_3Br_2S$; C, 47.11; H, 2.39; N, 9.56; Br, 27.27, S, 5.46. Found: C, 47.10; H, 2.40; N, 9.58; Br, 27.21, S, 5.43. Ir(cm^{-1}): 1720-1700, 1590, 1570. ^{1}H Nmr($CDCl_3$+DMSO-d_6, δ ppm): 8.05-7.7(8H, m, Ar-H), 7.45 (2H, d, J=10 Hz, C-7, C-8), 5.9 (2H, s, CH_2 at 4th position), 5.5 (2H, s, CH_2 at 6th position). Ms(m/z): 586(M+2, 7), 584(M^+ , 4), 401(M-COC_6H_4Br, 7), 388 (M-$CHCOC_6H_4Br$, 4), 278(M-$C_{12}H_4Br_2$,7),183(COC_6H_4Br.16). **5i**: R=$CH_2COC_6H_4NO_2(p)$. Yield, 63%; mp 237-240°C. Anal. Calcd for $C_{23}H_{14}N_6O_7S$; C, 53.28; H. 2.70; N, 16.21; S, 6.17. Found: C, 53.27; H, 2.68; N, 16.19; S, 6.14. Ir(cm^{-1}): 1715-1700, 1598, 1570. ^{1}H Nmr($CDCl_3$, δ ppm); 8.05-7.8 (8H, m, Ar-H), 7.6 (2H, d, J=10 Hz, C-7, C-8), 5.8 (2H, s, CH_2 at 4th position), 5.6 (2H, s, CH_2 at 6th position). Ms(m/z): 518(M^+ , 70), 368(M-$COC_6H_4NO_2$, 33), 355(M-$C_8H_5NO_3$, 21), 205(355-$C_7H_4NO_3$ .10). **5j**: R=$CH_2COC_6H_4(OCH_3)(p)$. Yield, 41%; mp 225-230°C. Anal. Calcd for $C_{25}H_{20}N_4O_5S$; C, 61.47; H, 4.09; N,

11.47; S, 6.56. Found: C, 61.49; H, 4.11; N, 11.47; S, 6.54. Ir(cm^{-1}): 1710-1690, 1600, 1585. ^{1}H Nmr(DMSO-d_6, δ ppm); 8.05-7.8(8H, m, Ar-H), 7.6 (2H, d, J=10 Hz, C-7, C-8), 5.7 (2H, s, CH_2 at 4th position), 5.4 (2H, s, CH_2 at 6th position), 3.9 (6H, s, OCH_3). Ms(m/z): 488(M^+, 28), 353 (M-$C_8H_7O_2$, 19), 340(M-$C_9H_8O_2$, 14), 205(340-$C_8H_7O_2$, 8).

5. Preparation of 6-Isopropenyl-4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one (**6**)

4,5-Diamino-2,1,3-benzothiadiazole, (**1**, 16.6 g, 0.1 mol), xylene (300 ml) and methyl acetoacetate (45 ml, 0.4 mol) were mixed and refluxed for 16 h. The reaction mixture was cooled to ambient temperature and made alkaline with 10% sodium hydroxide solution. The aqueous layer was separated and refluxed with a little activated charcoal and filtered. This solution was cooled to ambient temperature and was neutralised with 10% hydrochloric acid solution. The yellowish precipitate that separated was collected by filtration and dried. The product was purified from aq. sodium hydroxide solution followed by regeneration with acetic acid solution after carbon treatment. This experiment was also carried out in toluene and benzene. But low yields were obtained in benzene. Yield, 14.38 g (62%); mp 184-188°C. Anal. Calcd for $C_{10}H_8N_4OS$; C, 51.72; H, 3.45; N, 24.15; S, 13.79. Found: C, 51.70; H, 3.43; N, 24.12; S, 13.76. Ir (cm^{-1}): 3200-3250 (sh, NH), 1699 (C=O), 1605(C=N), 1574 (C=C). ^{1}H Nmr (DMSO-d_6, δ ppm): 13.8-13.0 (1H, s), 12.8 (1H, s), 7.95 (1H, d, J=8 Hz, C-8), 7.85 (1H, d, J=8 Hz, C-7), 3.3 (2H, s, CH_2), 2.3 (3H, s, CH_3). Ms(*m/z*) : 232 (M^+, 5%), 204 (M-CO, 5), 191 (M-C_3H_5, 50), 190 (M-C_3H_6, 100), 163 (190-CO, 12), 157 (191-SH,18).

6. Preparation of 4-Substistuted 6-Isopropenyl-4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-ones (**8a-c**).

General Procedure: A mixture of 6-isopropenyl-4*H*-imidazo[4,5-*e*][2,1,3]benzothiadiazol-5(6*H*)-one, (**6**, 2.32 g, 0.01 mol), sodium hydroxide (0.4 g, 0.01 mol), ethanol (100 ml) and water (10 ml) was refluxed for 15 min. Then the alkyl / aralkyl halide (0.01 mol) was added. The reaction mixture was refluxed for 3 h and then the solvent was distilled off. The residue left over was washed with 10% sodium hydroxide to remove unreacted compound (**6**). The remaining solid was recrystallised from aq. dioxan. **8a**: R=$CH_2COC_6H_4Cl(p)$. Yield, 46%; mp 192-194°C. Anal. Calcd for $C_{18}H_{13}N_4O_2ClS$; C, 56.17; H, 3.38; N, 14.56; Cl, 9.23; S, 8.32. Found: C, 56.15; H, 3.37; N, 14.53; Cl, 9.20; S, 8.30. Ir(cm^{-1}): 1730-1705, 1590, 1560. ^{1}H Nmr($CDCl_3$, δ ppm); 8.1-7.8(4H, m, Ar-H), 7.6(2H, d, C-7, C-8), 6.2(2H, s, CH_2 at 4th position), 2.70(2H, s, H_2C=C), 1.3(3H, s, CH_3). Ms(m/z): 386(M+2 , 3), 384(M^+, 10), 342(M-C_3H_6, 23), 314(342-CO, 5), 203(342-ClC_6H_4CO, 35), 139(ClC_6H_4CO, 100). **8b**: R=$CH_2COC_6H_4Br(p)$.

Yield, 52%; mp 174-184°C. Anal. Calcd for $C_{18}H_{13}N_4O_2BrS$; C, 50.36; H, 3.03; N, 13.06; Br, 18.62; S, 7.46. Found: C, 50.34; H, 3.07; N, 13.03; Br, 18.65; S, 7.48. Ir(cm^{-1}): 1750-1697, 1580, 1560. ^{1}H Nmr($CDCl_3$, δ ppm,): 8.3-7.8(6H, m, Ar-H), 6.1(2H, s, CH_2 at 4th position), 2.65 (2H, s, H_2C=C), 1.8(3H, s, CH_3). Ms(*m/z*): 428(M^+, 3), 430(M+2, 2.5), 386(M-C_3H_6, 39), 356(386-H_2CO, 5), 308(M-HBr, 5), 203 (386-COC_6H_4Br, 46), 183 (COC_6H_4Br, 100), 155(C_6H_4Br, 21). **8c**: R=$CH_2COC_6H_4$ NO_2(*p*). Yield, 43%; mp 186-188°C. Anal. Calcd for $C_{18}H_{13}N_5O_4S$; C, 54.68; H, 3.29; N, 17.72; S, 8.10. Found: C, 54.66; H, 3.27; N, 17.75; S, 8.12. Ir(cm^{-1}): 1725-1715, 1600, 1570. ^{1}H Nmr($CDCl_3$, δ ppm); 8.0-7.7(6H, m, Ar-H), 5.9 (2H, s, CH_2 at 4th position), 2.8 (2H, s, H_2C=C), 1.2 (3H, s, CH_3). Ms(m/z): 395 (M^+, 31), 349(M-NO_2, 11), 353 (M-C_3H_6, 18), 203(353-$COC_6H_4NO_2$, 21).

7. Preparation of 4-Substituted 4*H*-Imidazo[4,5-*e*][2,1,3] benzothiadiazol-5(6*H*)ones (**9a-c**).

General Procedure: A mixture of **8** (0.005 mol) and conc. hydrochloric acid (100 ml) was heated to 85-90°C and maintained at this temperature for 6 h and then cooled to afford a solid. This was collected by filtration and dried. The product was recrystallised from aq. dioxan. **9a**: R=$CH_2COC_6H_4Cl$(*p*). Yield, 55%; mp 241-242°C. Anal. Calcd for $C_{15}H_9N_4O_2ClS$; C, 52.25; H, 2.61; N, 16.25; Cl, 10.30; S, 9.29. Found: C, 52.21; H, 2.59; N, 16.26; Cl, 10.27; S, 9.30. Ir (cm^{-1}) : 3380 (sh, NH), 1710-1690(C=O), 1590, 1560. ^{1}H Nmr ($CDCl_3$, δ ppm): 8.1-8.2 (2H, d, J=10 Hz, 2H ortho to C=O), 8.0 (1H, d, J=8 Hz, C-8), 7.75-7.85 (1H, d, J=8 Hz, C-7), 7.5-7.65 (2H, d, J=10 Hz, 2H ortho to Cl), 6.3 (2H, s, CH_2), 2.9 (NH, br, s). Ms(*m/z*): 344 (M^+, 18), 342 (M-H_2, 36), 203 (342-ClC_6H_4CO, 30), 139 (ClC_6H_4CO, 100), 111($ClC_6H_4^+$, 23). **9b**: R=$CH_2COC_6H_4Br$(*p*). Yield, 58%; mp 233-234°C. Anal. Calcd for $C_{15}H_9N_4O_2BrS$; C, 46.28; H, 2.31; N, 14.39; Br, 20.54; S, 8.23. Found: C, 46.30; H, 2.33; N, 14.38; Br, 20.56; S, 8.25. Ir(cm^{-1}): 3420 (sh, NH), 1701(sh, C=O), 1585(sh, C=N, C=C). ^{1}H Nmr(DMSO-d_6, δ ppm): 8.2-7.9(6H, m, Ar-H), 6.55(2H, s, CH_2), 3.6(NH, br, s). Ms(*m/Z*): 386(M-2H, 75), 358(M-HCHO, 5), 308(M-HBr, 10), 279(308-CHO, 5), 203 (386-COC_6H_4Br, 64), 183(COC_6H_4Br, 96), 185(M+2 peak of 183, 100), 155(C_6H_4Br, 13). **9c**: R=$CH_2COC_6H_4NO_2$(*p*). Yield, 51%; mp 229-230°C. Anal. Calcd for $C_{15}H_9N_5O_4S$; C, 50.70; H, 2.53; N, 19.72; S, 9.01. Found: C, 50.71; H, 2.50; N, 19.75; S, 9.05. Ir(cm^{-1}): 3390(sh, NH), 1710(C=O), 1590. ^{1}H Nmr(DMSO-d_6, δ ppm): 8.1-7.7(6H, m, Ar-H), 6.3(2H, s, CH_2). Ms(*m/Z*): 355(M^+, 68), 325(M-HCHO, 16), 203(M-$C_7H_6NO_3$, 40), 175(203-CO, 7).

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