SHORT PAPER

J. Chem. Research (S), 2000, 496–498

Ortho amino carbonitriles as precursor for the synthesis of some novel heterocyclic compounds†

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Synthesis and characterisation of some new [1,2,4]triazoles 8,9 and 11 starting from a useful synthon 2-amino-5,6-dihydro-4*H*-benzo[3,4]cyclohepta[*b*]thiophene-1-carbonitriles have been reported.

A literature survey reveals that various 1,2,4-triazoles and the *N*-bridged heterocycles derived from them possess diverse pharmacological activities.[1,2] Prompted by these observations and in continuation of our work in the synthesis of biologically active nitrogen and sulfur containing heterocycles,[3] we now wish to report the conversion of the 2-amino-1-carbonitrile (**3**) into derivatives of a new heterocyclic system incorporating the pyrimidine moiety.

We envisage the 2-amino-1-carbonitrile **3** as a general precursor for the synthesis of a broad range of biologically active triazolo pyrimidines. The key intermediate **3** used in our experiments was readily prepared according to a described procedure[4] starting from the malononitrile **2**, which in turn was obtained from the ketone **1** under standard Knoevenagel conditions. Strong absorption of infrared peaks at 2210 and 3330 cm^{-1} clearly indicates the presence of nitrile and amino groups respectively in **3**. The carbonitrile **3** was reacted with triethyl orthoformate to yield the ethoxy methyleneamino derivative **4**. The structure of **4** was assigned by the presence of a triplet at δ 1.45 and a quartet at δ 4.50 corresponding to the protons of the ethoxy group in ^{1}H NMR, along with the expected signals for methylene and aryl hydrogen atoms.

Reaction of **4** with 4-chloroaniline in ethanol at room temperature effected cyclisation to give **5**. The IR spectrum of **5** showed the characteristic bands at 3250 (NH) and 1637 cm^{-1} (C=N) and the absence of C≡N band. Compound **5** underwent Dimroth rearrangement to the corresponding fused arylaminopyrimidine **6** on treatment with aq. NaOH. The Dimroth rearrangement in which alkyl and aryl groups apparently migrate from one of the ring nitrogens to the imino group of a 4-iminopyrimidine moiety has been reported in several cases.[5]

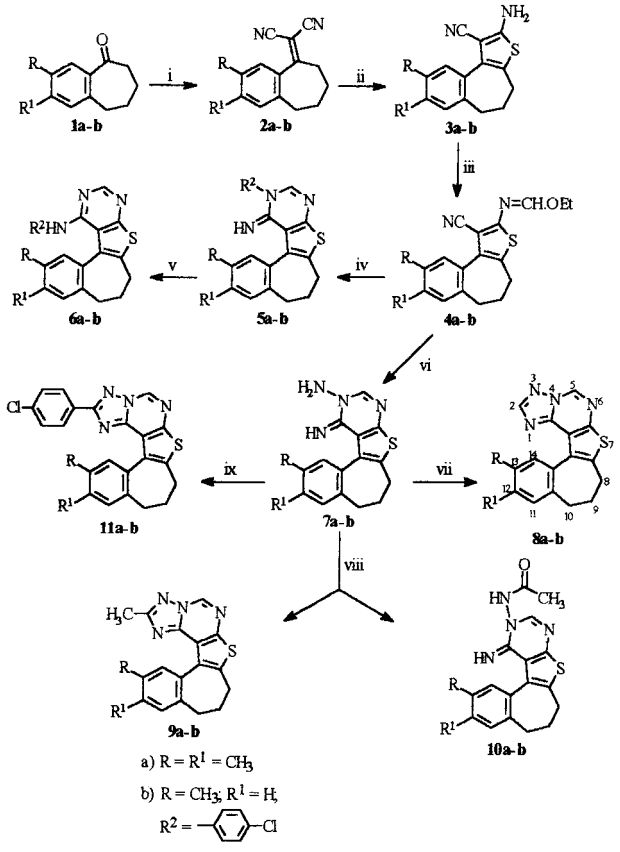
12-Imino-2,3-dimethyl-6,7,11,12-tetrahydro-5*H*-benzo[3′,4′]cyclohepta[2′,1′:4,5] thieno[2,3-*d*]pyrimidine-11-amine **7**, obtained by the reaction of **4** with hydrazine hydrate, was further converted into triazolo pyrimidine derivative **8** by treatment with triethyl orthoformate in dimethyl formamide. The formation of a triazole ring involving both amino and imino groups was evident by the absence of absorption bands due to either of these groups in the infrared spectrum of **8**. The ^{1}H NMR spectrum of **8** also showed the presence of two protons at δ 9.30 and 8.38 as singlets (at **2** and **5** positions) and the other aromatic protons appeared as a multiplet at δ 7.20–7.75.

Condensation of **7** with acetic anhydride in acetic acid yielded two crystalline compounds **9** and **10**. These were separated on a neutral alumina column followed by preparative TLC to give a major (more polar) and minor (less polar) product. The structures of the compounds **9** and **10** were assigned on the basis of the ^{1}H NMR spectra. The IR spectrum of **10** exhibited absorption bands at 3187 and 1660 cm^{-1} due to the -NH–CO– functionality. Reaction of **7** with 4-chlorobenzaldehyde yielded the pyrimidine derivative **11**. The structure of compounds **3–11** was confirmed by elemental analysis and spectral data.

Experimental

M.p.s are uncorrected. IR spectra are recorded on a Perkin Elmer FT IR 1605 spectrometer. ^{1}H NMR spectra are recorded in $CDCl_3$ on a Varian FT 80 A spectrometer with TMS as an internal standard and mass spectra are taken on a VG micromass 7070H mass spectrometer.

*2-(5-Dicyanomethylene-2,3-dimethyl-6,7,8,9-tetrahydro-5*H*-benzo[a]cyclohepten-5-ylidene)malononitrile* **(2a)**: 2,3-Dimethyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one[6] in ethanol was treated with malononitrile and triethyl amine as described.[4] The crude product **2a** (88%), which was used for next step without further purification. ν_{max} (film): 2208 (CN) cm^{-1}.



Reagents: (i) Malononitrile, Et_3N, EtOH, reflux; (ii) sulfur, morpholine, ethanol, reflux; (iii) Triethyl orthoformate, reflux; (iv) *p*-Cl-aniline, ethanol, R.T.; (v) 1N NaOH, 90°C; (vi) Hydrazine hydrate, R.T.; (vii) triethyl orthoformate, DMF, 90°C; (viii) Ac_2O, AcOH, reflux; (ix) *p*-chlorobenzaldehyde, pyridine, reflux.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

*2-(5-Dicyanomethylene-3-methyl-6,7,8,9-tetrahydro-5*H-*benzo[a]cyclohepten-5-ylidene)malononitrile* **(2b)**: Obtained as liquid, yield (87%), ν_{max} (film): 2210 (CN) cm^{-1}.

*2-Amino-8,9-dimethyl-5,6-dihydro-4*H-*benzo[3,4]cyclohepta[b] thiophene-1-carbonitrile* **(3a)**: Compound **3a** was prepared from **2a** (8.5 mmole), sulfur (0.285 g) and morpholine (five drops) in dry ethanol according to the procedure described[4] (92% yield), m.p. 98–100°C; ν_{max} (KBr): 3331, 3202 (NH_2), 2210 (CN) cm^{-1}; δ_H 2.20 (2H, m, 5-CH_2) 2.30 (6H, s, 2x CH_3), 2.45 (2H, t, 4-CH_2), 2.58 (2H, t, 6-CH_2), 4.65 [2H, br NH (exch.)], 7.00 (1H, s, 7-H) and 7.25 (1H, s, 10-H); *m/z* (rel intensity) 268 (M^+, 100), 253 (50), 238 (29), 165 (13), 119 (19), 83 (20), and 57 (25) [Found : C, 71.66; H, 5.94; N, 10.41. $C_{16}H_{16}N_2S$ requires C, 71.64; H, 5.97; N, 10.45%].

*2-Amino-9-methyl-5,6-dihydro-4*H-*benzo[3,4]cyclohepta[b] thiophene-1-carbonitrile* **(3b)**: yield (91%); m.p. 80–82°C; ν_{max} (KBr): 3333, 3200 (NH_2), 2212 (CN) cm^{-1}; δ_H 2.21 (2H, m, 5-CH_2), 2.32 (3H, s, -CH_3), 2.45 (2H, t, 4-CH_2), 2.62 (2H, t, 6-CH_2), 4.80 [2H, br, NH (exch.)] and 7.00–7.30 (3H, m, aromatic); *m/z* (rel intensity) 254 (M^+, 100), 239 (49), 224 (24), 152 (11), 60 (11) and 44 (61) [Found : C, 70.85; H, 5.48; N, 11.00. $C_{15}H_{14}N_2S$ requires C, 70.87; H, 5.51; N, 11.02%].

*2-[(E)-1-ethoxymethyleneamino]-8,9-dimethyl-5,6-dihydro-4*H-*benzo[3,4]cyclohepta[b]thiophene-1-carbonitrile* **(4a)**: A solution of **3a** (1.0 g, 3.73 mmole) in triethyl orthoformate (6 ml) was heated under reflux for 2 h and worked-up in the usual way. Recrystallised from petroleum ether to give **4a** (1.1g, 91%), m.p. 115–117°C; ν_{max} (KBr): 2216 (CN) cm^{-1}; δ_H1.45 (3H, t, CH_3), 2.25 (2H, m, 5-CH_2), 2.34 (6H, s, 2x-CH_3), 2.58 (4H, t, 4- & 6-CH_2), 4.50 (2H, q, OCH_2), 7.05 (1H, s, 7-H), 7.32 (1H, s, 10-H) and 8.04 (1H, s, N=CH); *m/z* (rel intensity) 324 (M^+, 42), 296 (23), 268 (100), 253 (63), 238 (35), 165 (16), 64 (23) and 57 (74) [Found: C, 70.34; H, 6.12; N, 8.68. $C_{19}H_{20}N_2OS$ requires C, 70.37; H, 6.17; N, 8.64%].

*2-[(E)-1-ethoxymethyleneamino]-9-methyl-5,6-dihydro-4*H-*benzo[3,4]cyclohepta[b]thiophene-1-carbonitrile* **(4b)**: yield (0.54g, 88%), m.p. 100-102°C; ν_{max} (KBr): 2212 (CN) cm^{-1}; δ_H: 1.42 (3H, t, CH_3), 2.25 (2H, m, 5-CH_2), 2.30 (3H, s, -CH_3), 2.58 (4H, t, 4 & 6-CH_2), 4.52 (2H, q, -OCH_2), 7.00–7.42 (3H, m, aromatic) and 8.00 (1H, s, N=CH); *m/z* (rel intensity) 310 (M^+, 100), 282 (26), 254 (35), 239 (39), 152 (12) and 57 (10) [Found : C, 69.64; H, 5.79; N, 9.10. $C_{18}H_{18}N_2OS$ requires C, 69.67; H, 5.81; N, 9.03%].

*11-(4-Chlorophenyl)-2,3-dimethyl-6,7,11,12-tetrahydro-5*H-*benzo[3′,4′]cyclohepta [2′,1′:4,5]thieno[2,3-*d*]pyrimidin-12-imine* **(5a)**: A mixture of **4a** (0.1g, 0.309 mmole), 4-chloroaniline (0.078g, 0.617 mmole) and absolute ethanol (2 ml) was stirred at room temperature overnight. After usual work-up, the crude product was recrystallised from petroleum ether / benzene yielded the product **5a** (0.115g, 92%); m.p. >270°C (decomp.); ν_{max} (KBr): 3290 (NH), 1637 (C=N) cm^{-1}; δ_H: 2.25-2.35 (2H, m, 6-CH_2), 2.40 (6H, s, 2x-CH_3), 2.60 (4H, t, 5 & 7-CH_2), 7.10-7.40 (6H, m, aromatic), 8.30 [1H, br, NH (exch.)] and 8.60 (1H, s, 10-H); *m/z* (rel intensity) 405 (M^+, 12), 407 (M^+ + 2, 4.5), 235 (25), 155 (23), 127 (30), 85 (55), 71 (74.5) and 57 (100) [Found : C, 68.10; H, 4.90; N, 10.34. $C_{23}H_{20}ClN_3S$ requires C, 68.15; H, 4.94; N, 10.37%].

*11-(4-Chlorophenyl)-2-methyl-6,7,11,12-tetrahydro-5*H-*benzo[3′,4′]cyclohepta [2′,1′:4,5]thieno[2,3-*d*]pyrimidin-12-imine* **(5b)**: yield 0.12g (94%), m.p. 172-174°C; ν_{max} (KBr): 3290 (NH), 1635 (C=N) cm^{-1}; δ_H: 2.25–2.35 (2H, m, 6-CH_2), 2.40 (3H, s, CH_3), 2.62 (4H, t, 5 & 7-CH_2), 7.10–7.45 (7H, m, aromatic), 8.32 [1H, br, NH (exch.)] and 8.60 (1H, s, 10-H); *m/z* (rel intensity) 391 (M^+, 60), 393 (M^+ + 2, 24), 390 (100), 254 (10), 127 (8), 85 (15), 71 (22), 57 (32) and 44 (31) [Found : C, 67.55; H, 4.54; N, 10.69. $C_{22}H_{18}ClN_3S$ requires C, 67.52; H, 4.60; N, 10.74%].

N*(12)-(4-Chlorophenyl)-2,3-dimethyl-6,7-dihydro-5*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[2,3-*d*]pyrimidin-12-amine* **(6a)**: The 12-imino compound **5a** (0.1 g) was suspended in 1N aqueous sodium hydroxide (5 ml) and then warmed at 90°C on a water bath for 48 h to give **6a** (50 mg, 50%); m.p. 110–112°C; ν_{max} (KBr): 3273 (NH), 1638 (C=N) cm^{-1}; δ_H: 2.25–2.35 (2H, m, 6-CH_2), 2.42 (6H, s, 2 × CH_3), 2.58 (4H, t, 5- & 7-CH_2), 7.10–7.40 (6H, m, aromatic), 8.05 [1H, br, NH (exch.)] and 8.70 (1H, s, 10-H); *m/z* (rel intensity) 405 (M^+, 95), 407 (M^+ + 2, 38), 404 (100), 185 (8), 85 (15), 71 (21), 57 (32) and 44 (59) [Found : C, 68.10; H, 4.90; N, 10.35. $C_{23}H_{20}ClN_3S$ requires C, 68.15; H, 4.94; N, 10.37%].

N*12-(4-Chlorophenyl)-2-methyl-6,7-dihydro-5*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[2,3-*d*]pyrimidin-12-amine* **(6b)**: Yield (35 mg, 35%), m.p. 118–120°C; ν_{max} (KBr): 3275 (NH), 1632 (C=N) cm^{-1}; δ_H: 2.20–2.30 (2H, m, 6-CH_2), 2.38 (3H, s, CH_3), 2.55 (4H, t, 5 & 7 -CH_2), 7.10–7.45 (7H, m, aromatic), 8.15 [1H, br, NH (exch.)] and 8.74 (1H, s, 10-H); *m/z* (rel intensity) 391 (M^+, 99), 393 (M^+ + 2, 38), 149 (22), 84 (100) and 57 (76) [Found: C, 67.54; H, 4.55; N, 10.68. $C_{22}H_{18}ClN_3S$ requires C, 67.52; H, 4.60; N, 10.74%].

*12-Imino-2,3-dimethyl-6,7,11,12-tetrahydro-5*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[2,3-*d*]pyrimidin-11-amine* **(7a)**: A mixture of **4a** (0.5g, 1.54 mmole) and hydrazine hydrate (2.5 ml) was stirred at room temperature for 45 min and worked-up in the usual way to give **7a** (0.42 g, 87%), m.p. 158–161°C; ν_{max} (KBr): 3327, 3300, 3215 (NH_2, NH) cm^{-1}; δ_H: 1.98–2.05 (2H, m, 6-CH_2), 2.15 (6H, s, 2x CH_3), 2.30 (2H, t, 7-CH_2), 2.55 (2H, t, 5-CH_2), 5.45 [2H, br, NH_2 (exch.)], 7.08 (1H, s, 4-H), 7.25 (1H, s, 1-H), 8.18 (1H, s, 10-H) and 8.30 [1H, br, NH (exch.)]; *m/z* (rel intensity) 310 (M^+, 13), 309 (22), 295 (100), 280 (44), 268 (24), 165 (30), 133 (23), 77 (22), 69 (36) and 57 (37) [Found: C, 65.80; H, 5.76; N, 18.10. $C_{17}H_{18}N_4S$ requires C, 65.81; H, 5.81; N, 18.06%].

*12-Imino-2-methyl-6,7,11,12-tetrahydro-5*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[2,3-*d*]pyrimidin-11-amine* **(7b)**: yield (0.425 g, 89%), m.p. 165–169°C; ν_{max} (KBr): 3325, 3300, 3220 (NH_2, NH) cm^{-1}; δ_H: 2.00–2.10 (2H, m, 6-CH_2), 2.25 (3H, s, -CH_3), 2.30 (2H, t, 7-CH_2), 2.58 (2H, t, 5-CH_2), 5.50 [2H, br, NH_2 (exch.)], 7.05-7.30 (3H, m, aromatic), 8.28 (1H, s, 10-H) and 8.32 [1H, br, NH (exch.)]; *m/z* (rel intensity) 296 (M^+, 11), 295 (16), 281 (98), 266 (100), 254 (60), 224 (33), 165 (20), 69 (23) and 57 (29) [Found: C, 64.82; H, 5.35; N, 18.90. $C_{16}H_{16}N_4S$ requires C, 64.86; H, 5.40; N, 18.92%].

*12,13-Dimethyl-9,10-dihydro-8*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[3,2-e] [1,2,4]triazolo[1,5-*c*]pyrimidine* **(8a)**: A mixture of compound **7a** (0.07 g, 0.22 mmole) triethyl orthoformate (0.27 ml) and dimethyl formamide (0.27 ml) was heated on a water bath for 4 h and worked-up in the usual way. Purification was by preparative TLC giving solid material **8a** (0.03 g, 41%), m.p. 122–125°C; λ_{max} (EtOH): 317 nm; δ_H: 2.40-2.48 (2H, m, 9-CH_2), 2.52 (6H, s, 2x CH_3), 2.72 (2H, t, 8-CH_2), 2.90 (2H, t, 10-CH_2), 7.20 (1H, s, 11-H), 7.70 (1H, s,14-H), 8.38 (1H, s, 5-H) and 9.30 (1H, s, 2-H); *m/z* (rel intensity) 320 (M^+, 100), 305 (25), 280 (24), 71 (37) and 57 (56) [Found : C, 67.45; H, 5.05; N, 17.45. $C_{18}H_{16}N_4S$ requires C, 67.50; H, 5.00; N, 17.50%].

*13-Methyl-9,10-dihydro-8*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5] thieno[3,2-*e*][1,2,4] triazolo[1,5-*c*]pyrimidine* **(8b)**: yield (0.035g, 56%), m.p. 105–106°C; λ_{max} (EtOH): 309 nm; δ_H: 2.40–2.48 (2H, m, 9-CH_2), 2.52 (3H, s, -CH_3), 2.72 (2H, t, 8-CH_2), 2.90 (2H, t, 10-CH_2), 7.20–7.35 (2H, d, 11 & 12-H), 7.70 (1H, s, 14-H); 8.38 (1H, s, 5-H) and 9.30 (1H, s, 2-H); *m/z* (rel intensity) 306 (M^+, 49), 291 (25), 85 (41), 71 (62), 57 (94) and 44 (100) [Found : C, 66.62; H, 4.52; N, 18.25. $C_{17}H_{14}N_4S$ requires C, 66.67; H, 4.57; N, 18.30%].

9a: *Reaction of 12-imino-2,3-dimethyl-6,7,11,12-tetrahydro-5*H-*benzo[3′,4′]cyclo-hepta[2′,1′:4,5]thieno[2,3-d]pyrimidin-11-amine* (**7a**) *with acetic anhydride*. The compound **7a** (0.093 g, 0.3 mmole), acetic anhydride (0.15 ml) and glacial acetic acid (1 ml) were heated under reflux together for 6h and worked-up in the usual way. It was a mixture of two compounds (TLC). The mixture was separated by preparative TLC (elution with 2% ethyl acetate, petroleum ether). The first band comprised *2,12,13-trimethyl-9,10-dihydro-8*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine* **9a** (40 mg, 43%), m.p. 158–160°C; λ_{max} (EtOH): 315 nm; δ_H: 2.30 (6H, s, 2x CH_3), 2.35–2.40 (2H, m, 9-CH_2), 2.60 (2H, t, 8-CH_2), 2.62 (3H, s, 2-CH_3), 2.80 (2H, t, 10-CH_2), 7.05 (1H, s, 11-H), 7.62 (1H, s, 14-H) and 9.10 (1H, s, 5-H); *m/z* (rel intensity) 334 (M^+, 11), 310 (16), 268 (41), 97 (16), 85 (44), 71 (64), 57 (100) and 44 (66) [Found : C,68.24; H, 5.35; N, 16.75. $C_{19}H_{18}N_4S$ requires C, 68.26; H, 5.39; N, 16.77%]. The second band (20 mg, 19%) was *N1-[12-imino-2,3-dimethyl-6,7,11,12-tetrahydro-5*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[2,3-*d*]pyrimidine-11-yl]acetamide* **10a**, m.p. 225–228°C, ν_{max} (KBr): 3236 (=NH), 3187 (NH), 1659 (-CO-NH) cm^{-1}; δ_H 2.10-2.20 (2H, m, 6-CH_2), 2.15 (3H, s, x-$COCH_3$), 2.40 (6H, s, 2x CH_3), 2.55 (4H, t, 5- & 7-CH_2), 7.02 (1H, s, 4-H), 7.24 (1H, s, 1-H), 7.65 [1H, br, =NH (exch.)], 8.35 (1H, s, 10-H) and 11.23 [1H, br, NH (exch.)]; *m/z* (rel intensity) 352 (M^+, 5), 348 (29), 334 (100), 319 (32), 71 (41), 57 (60) and 44 (83) [Found : C, 64.75; H, 5.65; N, 15.95. $C_{19}H_{20}N_4OS$ requires C, 64.77; H, 5.68; N, 15.91%].

*2,13-Dimethyl-9,10-dihydro-8*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine* (**9b)**: Yield (0.04 g, 41%), m.p. 145-148°C; λ_{max} (EtOH): 306 nm; δ_H: 2.32 (3H, s, CH_3), 2.35–2.40 (2H, m, 9-CH_2), 2.60 (2H, t, 8-CH_2), 2.60 (3H, s, 2-CH_3) 2.80 (2H, t, 10-CH_2), 7.05–7.55 (3H, m, aromatic) and 9.10 (1H, s, 5-H); *m/z* (rel intensity) 320 (M^+, 90), 305 (26), 148 (10), 97 (10), 84 (100) and 51 (47) [Found : C, 67.55; H, 5.07; N, 17.55. $C_{18}H_{16}N_4S$ requires C, 67.50; H, 5.00; N, 17.50%].

*N1-[12-imino-2-methyl-6,7,11,12-tetrahydro-5*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[2,3-*d*]pyrimidine-11-yl]acetamide* (**10b)**: Yield (0.02 g, 19.5%), m.p 210–214°C; ν_{max} (KBr): 3236 (=NH), 3185 (-NH), 1660 (-CO-NH) cm^{-1}; δ_H: 2.10-2.20 (2H, m, 6-CH_2), 2.25 (3H, s, -$COCH_3$), 2.35 (3H, s, -CH_3), 2.50 (4H, t, 5 & 7 -CH_2), 7.05–7.32 (3H, m, aromatic), 7.60 [1H, br, =NH (exch.)], 8.30 (1H, s, 10-H) and 11.20 [1H, br, NH (exch.)]; *m/z* (rel intensity) 338 (M^+, 10), 320 (8), 296 (24), 254 (31), 127 (17), 71 (99) and 57 (100) [Found: C, 63.85; H, 5.29; N, 16.50. $C_{18}H_{18}N_4OS$ requires C, 63.90; H, 5.32; N, 16.56%].

*2-(4-Chlorophenyl)-12,13-dimethyl-9,10-dihydro-8*H-*benzo[3′,4′]cyclohepta [2′,1′:4,5]thieno[3,2-*e*][1,2,4]triazolo [1,5-*c*]pyrimidine* **(11a)**: A mixture of **7a** (0.1g, 0.33 mmole) 4-chlorobenzaldehyde (0.046 g, 0.33 mmole) and pyridine (1 ml) was heated under reflux for 2.5 h. After usual work up afforded the oily compound which was purified by preparative TLC to give **11a** (30 mg, 41%), m.p. 155–158°C; δ_H: 2.30–2.32 (2H, m, 9-CH_2), 2.40 (6H, s, 2x CH_3), 2.60 (2H, t, 8-CH_2), 2.85 (2H, t, 10-CH_2), 7.10-8.20 (6H, m, aromatic) and 9.20 (1H, s, 5-H); *m/z* (rel intensity) 430 (M^+, 26), 432 (M^+ + 2, 10), 390 (50), 253 (41), 127 (36), 71 (99) and 57 (100) [Found: C, 66.95; H, 4.40; N, 13.00. $C_{24}H_{19}ClN_4S$ requires C, 66.98; H, 4.42; N, 13.02%].

*2-(4-Chlorophenyl)-13-methyl-9,10-dihydro-8*H-*benzo[3′,4′]cyclohepta[2′,1′:4,5]thieno[3,2-*e*][1,2,4]triazolo [1,5-*c*]pyrimidine* **(11b)**: Yield (43 mg, 31%), m.p. 148–150°C; δ_H: 2.28-2.30 (2H, m, 9-CH_2), 2.40 (3H, s, CH_3), 2.50 (2H, t, 8-CH_2), 2.80 (2H, t, 10-CH_2), 7.00–7.65 (7H, m, aromatic) and 9.1 (1H, s, 5-H); *m/z* (rel intensity) 416 (M^+, 45), 418 (M^+ + 2, 19), 376 (82), 278 (13), 149 (43), 85 (44), 71 (62) and 57 (100) [Found: C, 66.38; H, 4.05; N, 13.40. $C_{23}H_{17}ClN_4S$ requires C, 66.35; H, 4.09; N, 13.46%].

Received 23 April 2000; accepted 20 August 2000
Paper 00/291

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