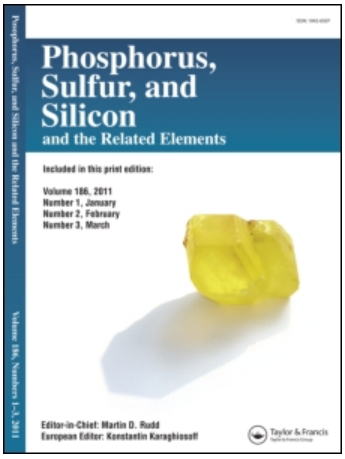

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESES OF CONDENSED TETRACYCLIC AND PENTACYCLIC THIAZOLOPYRIMIDINONES—A NEW CLASS[1]

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To cite this Article Babu, B. Ramesh , Ramana, D. V. and Ramadas, S. R.(1991) 'SYNTHESES OF CONDENSED TETRACYCLIC AND PENTACYCLIC THIAZOLOPYRIMIDINONES—A NEW CLASS[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 60: 3, 175 — 181
To link to this Article: DOI: 10.1080/10426509108036779
URL: http://dx.doi.org/10.1080/10426509108036779

Phosphorus, Sulfur, and Silicon, 1991, Vol. 60, pp. 175–181
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SYNTHESES OF CONDENSED TETRACYCLIC AND PENTACYCLIC THIAZOLOPYRIMIDINONES— A NEW CLASS[1]

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(Received August 15, 1990; in final form November 28, 1990)

Syntheses of tetracyclic and pentacyclic thiazolopyrimidinones (**3**, **6**, **11** and **16**) were obtained from the corresponding 2-aminothiazole derivatives (**1**, **4**, **10** and **13**) with simple methodology in fairly good yields.

Key words: 9-Methyl-6H,11H-[1]benzopyrao[4′,3′:4,5]thiazolo[3,2-a]pyrimidin-11-one; 9-methyl-6H,11H-[1]benzothiopyrano[4′,3′:4,5]thiazolo[3,2-a]pyrimidin-11-one; 7-amino-5,5-dimethyl-4H,5H-1,2,3-benzothiadiazolo[7,6-d]thiazole; 5,5,8-trimethyl-4H,5H-1,2,3-benzothiadiazolo[7′,6′:4,5]thiazolo[3,2-a]pyrimidin-10-one; 2-Amino-11H-naphtho[2′,1′:4,5]thiopyrano[4,3-d]thiazole; 9-methyl-6H,11H-naphtho[2″,1″:5′,6′]thiopyrano[4′,3′:4,5]thiazolo[3,2-a]pyrimidin-11-one.

INTRODUCTION

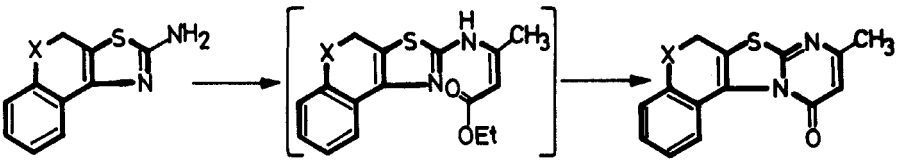
The syntheses of condensed thiazolopyrimidinones have attracted wide-spread interest of organic and medicinal chemists in recent years. These thiazolo[3,2-a]pyrimidinones[2–4] are well-known to display interesting biological properties such as antiinflammatory, antibacterial and antitumour. Thus, we wish to report herein the synthesis of tetracyclic (**3**, **6** and **11**) (Scheme I and II) and pentacyclic thiazolopyrimidinone derivative (**16**) (Scheme III) and with a view to study their biological properties. The methodology adopted for the syntheses of these thiazolopyrimidinones (**3** and **6**) (Scheme I) (**11**) (Scheme II) and (**16**) (Scheme III) is mainly based on the condensation of the structurally new types of 2-aminothiazole derivatives (**1**, **4**, **10** and **13**) with β-ketoesters under appropriate reaction conditions as discussed below.

RESULTS AND DISCUSSION

2-Amino-4H-[1]benzopyrano[4,3-d]thiazole[5] (**1**) (Scheme I), is condensed with ethyl acetoacetate (EAA) in the presence of catalytic amount of *p*-toluenesulfonic acid (PTS) in refluxing toluene obtained a light yellow solid of tetracyclic thiazolopyrimidinone derivative **3**, in 48% yield. All attempts to isolate the intermediate uncyclized ester **2** were not successful even in different experimental conditions.

Similarly, the synthesis of tetracyclic thiazolopyrimidinone derivative, 9-methyl-6H,11H-[1]benzothiopyrano[4′,3′:4,5]thiazolo[3,2-a]pyrimidin-11-one (**6**) (Scheme I) was achieved from 2-aminothiazole derivative[5] **4**, in 37% yield.

Quite recently Britton and co-workers[6] have claimed that A-ring-fused steroidal[3,2-d]-1,2,3-thiadiazoles exhibited male contraceptive activity. Prompted by

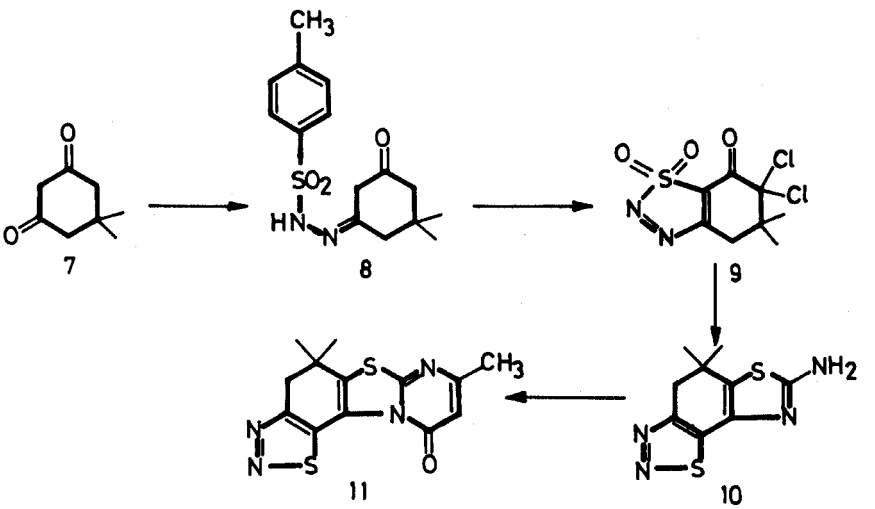


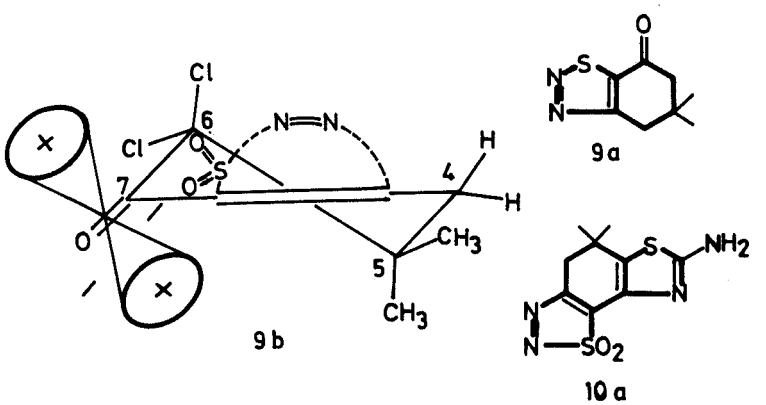
1, x = o
4, x = s

2, x = o
5, x = s

3, x = o
6, x = s

Scheme - I





Scheme - II

this observation, the total synthesis of tetracyclic heterocyclic system, 5,5,8-trimethyl-4H,5H-1,2,3-benzothiadiazolo[7′,6′:4,5]thiazolo[3,2-a]pyrimidin-10-one (**11**) was achieved as outlined in Scheme II.

With a view to construct the desired 1,2,3-thiadiazole ring system of the type

9a, the general procedure reported by Hurd and Mori[7] was adopted. Thus dimedone (**7**), on treatment with *p*-toluenesulfonylhydrazine in ethanol containing a few drops of conc. hydrochloric acid gave the corresponding monotosylhydrazone[8] **8**. Treatment of **8**[8] with thionyl chloride gave surprisingly the dichloro derivative of the thiadiazole derivative, 6,6-dichloro-5,5-dimethyl-4,5,6,7-tetrahydro-7-oxo-1,2,3-benzothiadiazole 1,1-dioxide (**9**), in 45% yield. The ^{1}H-nmr (400 MHz) showed a AB-quartet at δ 3.52 (A) and 3.63 (B) of the methylene protons at C-4. The observed magnetic nonequivalence of the methyl groups at C-5 and also of the methylene protons at C-4 is in keeping with the stereochemistry of the molecular model of **9b**. The anisotropy effect of the C=O group and the ring current effect of the adjacent heterocyclic moiety (1,2,3-thiadiazole) appear to be responsible for the observed magnetic nonequivalence of the methyl and methylene protons in **9**.

It is rather surprising to note that the product **9** isolated in this reaction is different from the anticipated product **9a**. It is quite difficult to offer a suitable explanation for this observation. But it is believed that excess thionyl chloride used in the experiment might have caused the observed chlorination of the heterocyclic ketone in its α-position to the ketonic function.

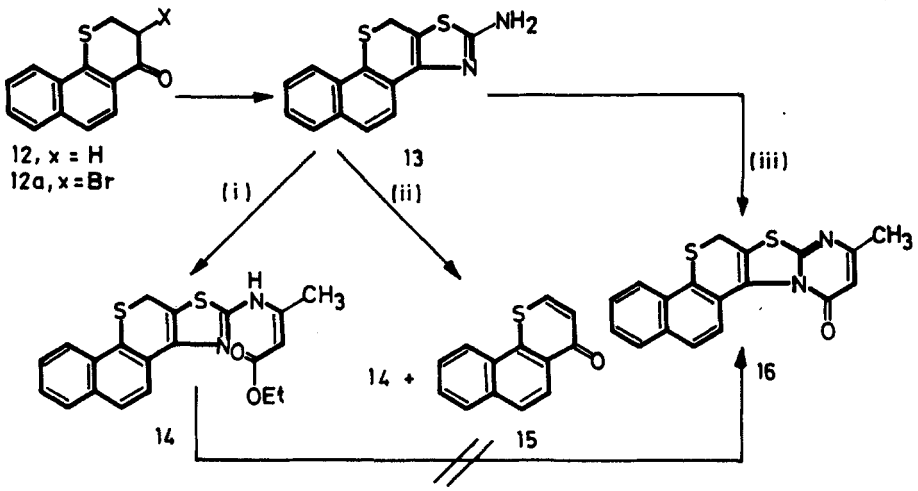
The next step in the envisaged synthetic sheme is to convert the dichloro keto derivative **9** into the desired 2-aminothiazole derivative **10**. Condensation of dichloro-1,2,3-thiadiazole derivative **9** with excess thiourea in refluxing ethanol afforded 7-amino-5,5-dimethyl-4H,5H-1,2,3-benzothiadiazolo[7,6-d]thiazole (**10**) in 52% yield.

It is worth pointing out here that the expected product in this reaction corresponds to **10a**. However, the spectral data revealed that the actual structure possessed by the product isolated in this experiment corresponds to **10** only. This appears to be rather an interesting transformation of 1,2,3-thiadiazole 1,1-dioxide **9** to the corresponding tricyclic heterocycle **10** by thiourea is rather unusual but quite noteworthy. It is also pointed out that the observed reduction by thiourea appears to be unique to this particular system only as revealed from our extensive experiments carried out with other simpler sulfones (acyclic and cyclic). In the majority of the cases showed such a facile conversion of a sulfone to sulfide with thiourea was not observed. Therefore the above unusual observation would not be generalized for the reduction of sulfones to sulfides.

Condensation of the 2-aminothiazole derivatives **10** with EAA in the presence of PTS in refluxing toluene afforded the tetracyclic thiazolopyrimidinone derivative **11**, in 36% yield.

Till date there has been no report on the total synthesis of pentacyclic thiazolopyrimidinone derivatives, we wish to report herein the first convenient method for the synthesis of pentacyclic thiazolopyrimidinone derivative, 9-methyl-6H,11H-naphtho[2″,1″:5′,6′]thiopyrano[4′,3′:4,5]thiazolo[3,2-a]pyrimidin-11-one (**16**) (Scheme III) by adopting the same methodology as mentioned in Scheme II.

The starting material, 1-oxo-4-thia-1,2,3,4-tetrahydrophenanthrene (**12**), required for the synthesis of the key-intermediate tetracyclic 2-aminothiazole **13**, was prepared in accordance with the reported procedure.[9] The above-mentioned tricyclic ketone[9] **12** was converted into the desired 2-aminothiazole derivative, 2-amino-11H-naphtho[2′,1′:5,6]thiopyrano[4,3-d]thiazole (**13**) in accordance with the procedure reported in our preliminary communication.[1c]



Scheme - III

In order to obtain the target molecule (**16**), three different conditions have been attempted. However, the target molecule (**16**) was successfully obtained in 40% yield without encountering the intermediates under the conditions stated in (iii).

(i) Condensation of tetracyclic 2-aminothiazole derivative (**13**) with EAA in presence of catalytic amount of PTS in refluxing toluene was attempted and in this case the product isolated was identified as the intermediate ester, ethyl Z-3-(11H-naphtho[2',1':5,6]thiopyrano[4,3-d]thiazol-2-ylamino)-2-butenoate (**14**), in 30% yield.

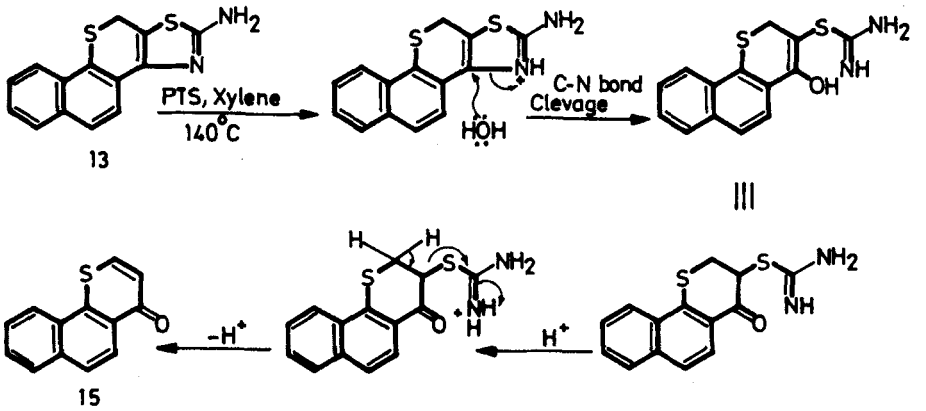
Subsequent attempts in separate experiments to effect the cyclization of the crotonate ester **14** employing (PTS) or boron trifluoride etherate or phosphorus oxychloride in refluxing toluene were all unsuccessful in furnishing the expected pentacyclic thiazolopyrimidinone derivative **16** and in each case the starting material **14** was recovered unchanged.

(ii) In another experiment, attempted condensation of tetracyclic 2-aminothiazole derivative **13** with EAA in the presence of catalytic amount of PTS in refluxing xylene yielded crotonate ester derivative **14** (23%) and also surprisingly the tricyclic heterocyclic ketone **15** in 16% yield. The most interesting aspect of this condensation reaction is the formation of the compound **15**. Its formation was rationalized by a probable mechanism as discussed in Scheme IV.

(iii) In our last attempt, condensation of the tetracyclic 2-aminothiazole derivative **13** with EAA in the presence of a large excess of PTS in refluxing toluene afforded directly thiazolopyrimidinone derivative **16** in 40% yield.

In summary, the methodology devised is simple and efficient for the construction of tetracyclic and pentacyclic thiazolopyrimidinones (**3**, **6**, **11** and **16**) starting from the corresponding 2-aminothiazole derivatives (**1**, **4**, **10** and **13**) respectively.

The intermediates and the title compounds were submitted for biological evaluation, such as antifertility and antitumour properties; results are awaited and will be reported elsewhere.



Scheme - IV

EXPERIMENTAL

Melting points were taken using a Toshiba melting point apparatus and are uncorrected. Hexane and petroleum ether, unless otherwise stated, refer to the fraction boiling at 60–80°. Infrared spectra were recorded using Perkin Elmer grating infrared spectrophotometer, model 1310. ^{1}H-Nmr spectra were recorded with Varian EM 390-90 MHz and Brucker 400 MHz spectrometers using TMS as the internal standard. The chemical shifts are reported in δ values. The ^{13}C-NMR (both proton noise decoupled and attached proton) spectra were obtained at 25.2 MHz in the Fourier Transform (FT) mode on Varian XL 200 and Brucker WP 100 FT NMR spectrometers. Mass spectra were recorded using Varian MAT CH7 and Finnigan MAT mass spectrometers.

9-Methyl-6H,11H-[1]benzopyrano[4',3':4,5]thiazolo[3,2-a]pyrimidin-11-one (**3**). 2-Amino-4H-[1]benzopyrano[4,3-d]thiazole[5] (**1**) (2.04 g, 10 mmol), ethyl acetoacetate (1.30 g, 10 mmol) and *p*-toluenesulfonic acid (0.285 g, 1.5 mmol) were dissolved in toluene (60 mL) and the solution was refluxed using a Dean-Stark water separator for 36 h. The reaction mixture was cooled, washed with water (3 × 25 mL) and dilute hydrochloric acid (2N) (3 × 25 mL) and the resulted organic layer was concentrated to give a dark brown solid. The residue was passed through a silicagel column (90 g) with an eluant of benzene-ethyl acetate (1:1) to afford a purified material as a yellow solid, which on recrystallization from chloroform and petroleum ether (9:1) gave the pure product of tetracyclic thiazolopyrimidinone derivative **3** (1.572 g) as a light yellow solid, mp 170–171°C, in 48% yield, ir (KBr): ν_{max} 1680, 1600, 1570, 1490 and 1390 cm^{-1}; ^{1}H-nmr($CDCl_3$): δ 2.29(s, 3H, methyl at C-9), 5.2(s, 2H, methylene at C-6), 6.15(s, 1H, olefinic proton at C-10) and 6.9–7.9(m, 4H, aromatic protons), ms(m/z): 270(M^+, 100), 269(43), 242(9), 241(18), 227(23), 203(18), 188(7), Anal. calcd. for $C_{14}H_{10}N_2O_2S$: C,62.22; H,3.70. Found: C,62.03; H,3.80.

9-Methyl-6H,11H-benzothiopyrano[4',3':4,5]thiazolo[3,2-a]pyrimidin-11-one (**6**). 2-Amino-4H-[1]benzothiopyrano[4,3-d]thiazole[5] **4** (2.20 g, 10 mmol) and ethyl acetoacetate (1.30 g, 10 mmol) were refluxed in toluene (60 mL) containing catalytic amount of *p*-toluenesulfonic acid (0.285 g, 1.5 mmol) using a Dean-Stark water separator for 20 h and the reaction mixture was worked-up as mentioned in the above experiment, gave a dark brown solid, which on chromatographic purification over silicagel (90 g) from benzene-ethyl acetate (8:2) eluates the tetracyclic thiazolopyrimidinone derivative **6** (1.80 g), followed by recrystallization from chloroform-petroleum ether (40–60°) (10:1) mixture gave pure sample of **6** (1.286 g), as a brown solid, mp 158–160° in 37% yield. ir(KBr): ν_{max} 1665, 1670, 1490 and 1400 cm^{-1}; ^{1}H-nmr($CDCl_3$): δ 2.4(s, 3H, methyl at C-9), 3.8(s, 2H, methylene at C-6), 6.17(s, 1H, olefinic proton) and 7.2–7.9(m, 4H, aromatic protons); ms(m/z): 286(M^+, 100), 285(28), 258(19), 257(37), 243(18), 219(10), Anal. calcd. for $C_{14}H_{10}N_2OS_2$: C,58.74; H,3.49. Found: C,58.52; H,3.42.

6,6-Dichloro-5,5-dimethyl-4,5,6,7-tetrahydro-7-oxo-1,2,3-benzothiadiazole 1,1-dioxide (**9**). To a suspension of monotosylhydrazone of dimedone[8] **8** (9.24 g, 30 mmol) in dry methylene chloride (150 mL), was added dropwise thionyl chloride (9.2 mL, 100 mmol) at room temperature and was stirred for 36 h, during this period the reaction mixture became dark red in color. The solvent and the excess thionyl

chloride were removed under reduced pressure, the residue was chromatographed over silicagel (150 g) (60–120 mesh), initially hexane eluates furnished the expected *p*-toluenesulfonyl chloride (5.12 g, 46%). Ethyl acetate-hexane (1:9) eluates gave the dichloro derivative of thiadiazole **9**, as a yellow crystalline solid, followed by recrystallization from hexane-ethyl acetate (9:1) mixture gave dichloro thiadiazole derivative **9** (4.752 g), as a pale yellow crystal, mp 138–139°C, in 45% yield, ir(KBr): ν_{max} 1710, 1300, 1150 cm^{-1}. ^{1}H-nmr($CDCl_3$): δ 1.3(s, 3H, methyl at C-5), 1.6(s, 3H, methyl at C-5), 3.52 (A) and 3.63 (B) [AB-quartet, 2H, methylene at C-4, J_{AB} = 18 Hz], ^{13}C-nmr($CDCl_3$): δ 25.17, C-5 Me; 25.78, C-5 Me; 37.96, C-4; 46.14, C-5; 92.0, C-6; 141.76 olefinic carbons and 162.38, C-7, ms(m/z): 283 (M^+, 7%), 247(13), 219(12), 191(9), 183(8), 155(18), 133(100), Anal. calcd. for $C_8H_8N_2O_3Cl_2S$: C,33.92; H,2.83. Found: C,33.85; H,2.81.

7-Amino-5,5-dimethyl-4H,5H-1,2,3-benzothiadiazolo[7,6-d]thiazole (**10**). A solution of dichloro derivative of thiadiazole **9** (1.41 g, 5 mmol) and thiourea (0.76 g, 10 mmol) was refluxed in ethanol for 4 h. Ethanol was evaporated and the reaction mixture stirred with 10% solution of potassium carbonate for 30 minutes, the resulting solid filtered off, washed several times with water and 10% solution of sodium metabisulphite and dried. Recrystallization from ethanol furnished the analytically pure sample of thiazole derivative **10** (1.075 g) as a yellow crystalline solid, mp 223–225°C, in 52% yield, ir(KBr): ν_{max} 3400, 3200, 1640, 1540, 1480 cm^{-1}, ^{1}H-nmr (DMSO-d_6): δ 1.3(s, 6H, *gem*-dimethyl at C-5), 3.2(s, 2H, methylene at C-4) and 6.2(broad s, 2H, —NH_2, exchangeable with D_2O), ms(m/z): 238(M^+, 59%), 223(73), 210(1), 195(100), 168(13), 153(34), 109(13), Anal. calcd. for $C_9H_{10}N_4S_2$: C,45.38; H,4.20. Found: C,45.12; H,4.16.

5,5,8-Trimethyl-4H,5H-1,2,3-benzothiadiazolo[7',6':4,5]thiazolo[3,2-a]pyrimidin-10-one (**11**). Tricyclic 2-aminothiazole derivative **10** (0.952 g, 4 mmol), ethyl acetoacetate (0.52 g, 4 mmol) and *p*-toluenesulfonic acid (0.190 g, 1 mmol) were refluxed in toluene (20 mL) for 15 h using a Dean-Stark water separator. The reaction mixture was cooled to room temperature, washed with water (3 × 20 mL) and dilute hydrochloric acid (2N) (3 × 20 mL). The resulting organic layer was concentrated under reduced pressure to furnish a brown solid, which on chromatographic purification over silicagel (30 g) followed by recrystallization from benzene-ethyl acetate (8:2) mixture gave the pure product of tetracyclic thiazolopyrimidinone derivative **11** (0.506 g), as a yellow solid, mp 196–198°C, in 36% yield, ir(KBr): ν_{max} 1665 and 1580 cm^{-1}; ^{1}H-nmr($CDCl_3$): δ 1.3(s, 6H, methyl at C-5), 2.2(s, 3H, methyl at C-8), 3.2(s, 2H, methylene at C-4) and 5.85(s, 1H, olefinic proton at C-9), ^{13}C-nmr($CDCl_3$): δ 23.7, C-8 Me; 27.9, C-5 Me_2; 35.6, C-5; 37.2, C-4; 105.7, C-9; 123.14–161.1, olefinic carbons and 163.9, C-10, ms(m/z): 304(M^+, 51), 276(95), 275(27), 261(100), 243(44), 153(41), 109(24), Anal. calcd. for $C_{13}H_{12}N_4OS_2$: C,51.32; H,3.95. Found: C,51.65; H,3.87.

2-Amino-11H-naphtho[2',1':4,5]thiopyrano[4,3-d]thiazole (**13**). Tricyclic α-bromoketone[10] **12a** (2.92 g, 10 mmol) and thiourea (0.76 g, 10 mmol) were refluxed in ethanol (40 mL) for 4 h. Ethanol was evaporated and the residue stirred with 10% potassium carbonate solution (50 mL) for 1 h, the resulting solid was filtered, washed with water and 10% sodium metabisulphite solution and dried. Recrystallization of the solid from ethanol furnished the 2-aminothiazole derivative **13** (1.125 g) as brown solid, mp 225°C (dec), in 45% yield, ir(KBr): ν_{max} 3300, 1620, 1605, 1510, 1450, 1420, 1380 cm^{-1}, ^{1}H-nmr(DMSO-d_6): δ 3.9(s, 2H, $S\underline{CH_2}$), 6.9–7.6(m, 6H, aromatic protons) and 9.5–9.7(broad s, 2H, NH_2, disappeared on D_2O exchange), ms(m/z): 270(M^+, 99%), 269(100), 268(92), 196(16), Anal. calcd. for $C_{14}H_{10}N_2S_2$: C,62.20; H,3.70. Found: C,62.53; H,3.84.

Ethyl (Z)-3-(11H-naphtho[2',1':5,6]thiopyrano[4,3-d]thiazol-2-ylamino)-2-butenoate (**14**). Tetracyclic 2-aminothiazole **13** (0.540 g, 2 mmol), ethyl acetoacetate (0.260 g, 2 mmol) and *p*-toluenesulfonic acid (0.045 g, 0.4 mmol) were dissolved in toluene (60 mL) and the solution was refluxed for 48 h using a Dean-Stark apparatus for continuous removal of water. The reaction mixture was cooled, washed with water (3 × 20 mL) and the organic layer was concentrated under reduced pressure to give thick brown solid, which on chromatographed over silicagel (100 g) followed by recrystallization from benzene-hexane (1:1) to furnish the pure sample of crotonate ester **14** (0.239 g), as a brown solid, mp 180–181°C, in 30% yield, ir(KBr): ν_{max} 3300, 1680, 1660 cm^{-1}, ^{1}H-nmr($CDCl_3$): δ 2.3(s, 3H, methyl at =C—CH_3), 3.8(s, 2H, —SCH_2), 4.0(q, 2H, —$CO_2\underline{CH_2}CH_3$), 1.3(t, 3H, —$CO_2CH_2\underline{CH_3}$, J = 6 Hz), 6.0(s, 1H, —NH, disappeared on D_2O exchange), Anal. calcd. for $C_{20}H_{18}N_2O_2S_2$: C,62.83; H,4.71. Found: C,62.59; H,4.54.

Preparation of crotonate ester (**14**) and 7,8-benzothiachrome (**15**) from tetracyclic 2-aminothiazole derivative (**13**). Tetracyclic 2-aminothiazole **13** (0.540 g, 2 mmol), ethyl acetoacetate (0.260 g, 2 mmol) and *p*-toluenesulfonic acid (0.045 g, 0.4 mmol) were dissolved in dry xylene (60 mL) and the solution was refluxed for 40 h using a Dean-Stark water separator. The resulting product was worked-up as explained in the above experiment to afford a thick brown gum, which on chromatographic separation

over silicagel (100 g) gave from benzene-hexane (1:1) eluates the crotonate ester **14** (0.184 g) in 23% yield. The benzene eluates furnished the tricyclic ketone, 7,8-benzothiachrome (**15**) (0.086 g), as a yellow solid, mp 145–147°C (reported,[11] mp 149–149.5°C) in 16% yield, ir(KBr) for **15**: ν_{max} 1610, 1450, 1380, 800 cm^{-1}, ^{1}H-nmr($CDCl_3$): δ 6.85(d, 1H, —SCH=CHCO, J = 10 Hz), 8.15(d, 1H, —SCH=CHCO, J = 10 Hz) and 7.2–8.05(m, 6H, aromatic protons).

9-Methyl-6H,11H-naphtho[2",1":5',6']thiopyrano[4',3':4,5]thiazolo[3,2-a]pyrimidin-11-one (**16**). 2-Amino-11H-naphto[2',1':5,6]thiopyrano[4,3-d]thiazole (**14**) (0.540 g, 2 mmol), ethyl acetoacetate (0.260 g, 2 mmol) and *p*-toluenesulfonic acid (0.190 g, 1 mmol) were dissolved in toluene (50 mL) and the solution was refluxed using a Dean-Stark water separator for 50 h. The resulting product was worked-up as explained in the above experiment to furnish a dark brown gum, which on chromatographic purification over silicagel from benzene-ethyl acetate (8:2) eluates and followed by recrystallization from chloroform yielded the pentacyclic thiazolopyrimidinone **16** (0.294 g), as a yellow solid, mp 213–215°C, in 40% yield, ir(KBr): ν_{max} 1670, 1560, 1480 and 1390 cm^{-1}, ^{1}H-nmr($CDCl_3$): δ 2.3(s, 3H, methyl at C-9), 3.6(s, 2H, methylene at C-6), 5.95(s, 1H, olefinic proton at C-10) and 6.9–7.95(m, 6H, aromatic protons), ms(m/z): 336(M^+, 100), 335(22), 308(9), 307(26), 293(8), 269(3), 254(6), HRMS(m/z): 336.0396 ($C_{18}H_{12}N_2OS_2$ requires 336.0519); Anal. Calcd. for $C_{18}H_{12}N_2OS_2$: C,64.28; H,3.57. Found: C,64.15; H,3.46.

ACKNOWLEDGEMENT

We wish to thank Department of Science and Technology (DST), India for the financial support and Dr. Kurt L. Loening for the systematic nomenclature of the ring systems. We are also thankful to Prof. H. J. C. Jacobs, Leiden University, Leiden for the high resolution proton nmr and mass spectral data.

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