# 2,6-Diaryl-4,4-disubstituted-4*H*-thiopyran: Source for Spiro Heterocycles



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The 1,5-diaryl-3,3-disubstituted-1,5-pentanedione on reaction with ammonium acetate, phosphorus pentoxide and phosphorus pentasulfide gave respective 1,4-dihydropyridine, 4*H*-pyran and 4*H*-thiopyran. Novel spiro heterocycles have been obtained by the cyclocondensation of 4*H*-thiopyran with hydrazine, hydroxylamine, urea and thiourea.

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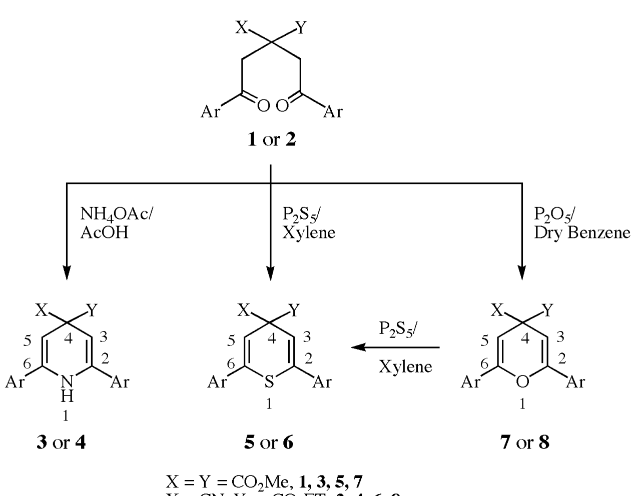
As a result of our sustained efforts in the search for new and versatile multi-functional reactive intermediates, recently we have reported the preparation of 1,5-diaryl-3,3-disubstituted-1,5-pentanediones **1** and **2** by the reaction of phenacyl bromide with dimethyl malonate and ethylcyano acetate [1]. The presence of dicarbonyl functionality in **1** and **2** enabled us to incorporate N, O and S as heteroatoms in them [2]. This gave scope for us to design and develop hitherto unknown spiro heterocycles by exploiting the *gem* diester or cyano ester groups of 1,4-dihydropyridine (**3** and **4**), 4*H*-thiopyran (**5** and **6**) and 4*H*-pyran (**7** and **8**). In fact, during the last decade we were actively involved in the syntheses of several spiro-heterocycles [3]. In further development of this synthetic strategy, we have now considered the reactivity of the 2,6-diaryl-4,4-disubstituted-4*H*-thiopyran(**5** and **6**) with hydrazine, hydroxylamine, urea and thiourea.

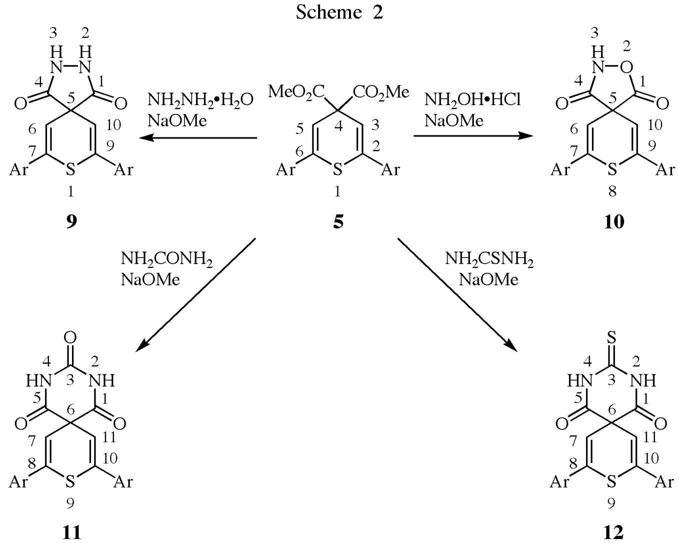
The synthetic method involves the reaction of 1,5-diaryl-3,3-dimethoxycarbonyl-1,5-pentanedione (**1**) or 1,5-diaryl-3-cyano-3-ethoxycarbonyl-1,5-pentanedione (**2**) with ammonium acetate in acetic acid, phosphorus pentasulfide in xylene and phosphorus pentoxide in dry benzene under reflux conditions to obtain 2,6-diaryl-4,4-dimethoxycarbonyl-1,4-dihydropyridine (**3**) or 2,6-diaryl-4-cyano-4-ethoxycarbonyl-1,4-dihydropyridine (**4**), 2,6-diaryl-4,4-dimethoxycarbonyl-4*H*-thiopyran (**5**) or 2,6-diaryl-4-cyano-4-ethoxycarbonyl-4*H*-thiopyran (**6**) and 2,6-diaryl-4,4-dimethoxycarbonyl-4*H*-pyran (**7**) or 2,6-diaryl-4-cyano-4-ethoxycarbonyl-4*H*-pyran (**8**) respectively (see Scheme 1 and Table 1) . Displacement of the oxygen atom in **7** or **8** on treatment with excess phosphorus pentasulfide in boiling xylene also gave **5** or **6**. The absence of carbonyl absorption (ArCO) around 1690 in IR spectra of **3-8** indicated their formation. Further **3** or **4** showed a band around 3350-3450 for (NH). The $^1$H NMR spectra of **3-8** showed a singlet in the region 5.22 – 5.86, which accounts for $C_3$-H and $C_5$-H protons. However in case of **3** and **4** a singlet was observed around 9.02 - 9.20 for N*H* which disappeares on deuteration. The $^{13}$C NMR spectra of **3-8** exhibited resonance signals at 142.15 – 152.28 ($C_2$ and $C_6$), 91.78 – 120.54 ($C_3$ and $C_5$) and 41.24 – 45.67 ($C_4$) which also support their structures (Table 3). The cyclocondensation of **5** with hydrazine, hydroxylamine, urea and thiourea in the presence of sodium methoxide resulted in the formation of 7,9-diaryl-8-thia-2,3-diaza-spiro[4,5]deca-6,9-diene-1,4-dione (**9**), 7,9-diaryl-2-oxa-8-thia-3-aza-spiro[4,5]deca-6,9-diene-1,4-dione (**10**), 8,10-diaryl-9-thia-2,4-diaza-spiro[5,5]undeca-

Scheme 1




Ar a) $C_6H_5$, b) 4-OMe$C_6H_4$, b) 4-Cl$C_6H_4$,

Scheme 2




Ar a) $C_6H_5$, b) 4-OMe$C_6H_4$, c) 4-Cl$C_6H_4$

Table 1

Physical Properties for Compounds **3-8**

| Comp. | M.P (°C) | Yield (%) | Molecular formula (Molecular weight) | Calcd. (Found) % C | H | N |
|---|---|---|---|---|---|---|
| **3a** | 168-169 | 68 | $C_{21}H_{19}NO_4$ 349.38 | 72.19 (72.33) | 5.48 (5.54) | 4.01 (3.97) |
| **3b** | 182-183 | 71 | $C_{23}H_{23}NO_6$ 409.43 | 67.47 (67.25) | 5.66 (5.78) | 3.42 (3.57) |
| **3c** | 148-149 | 64 | $C_{21}H_{17}Cl_2NO_4$ 418.27 | 60.30 (60.43) | 4.10 (4.16) | 3.35 (3.19) |
| **4a** | 152-153 | 66 | $C_{21}H_{18}N_2O_2$ 330.38 | 76.34 (76.50) | 5.49 (5.53) | 8.48 (8.29) |
| **4b** | 170-171 | 69 | $C_{23}H_{22}N_2O_4$ 390.43 | 70.75 (70.62) | 5.68 (5.72) | 7.17 (7.29) |
| **4c** | 132-133 | 62 | $C_{21}H_{16}Cl_2N_2O_2$ 399.27 | 63.17 (63.08) | 4.04 (4.12) | 7.02 (7.13) |
| **5a** | 181-182 | 40 57* | $C_{21}H_{18}O_4S$ 366.43 | 69.83 (69.70) | 4.95 (5.02) | - |
| **5b** | 192-194 | 35 51* | $C_{23}H_{22}O_6S$ 426.48 | 64.77 (64.66) | 5.20 (5.07) | - - |
| **5c** | 168-169 | 38 59* | $C_{21}H_{16}Cl_2O_4S$ 435.32 | 57.94 (57.84) | 3.70 (3.79) | - |
| **6a** | 158-159 | 42 62* | $C_{21}H_{17}NO_2S$ 347.43 | 72.59 (72.42) | 4.93 (4.97) | 4.03 (4.16) |
| **6b** | 172-173 | 39 50* | $C_{23}H_{21}NO_4S$ 407.48 | 67.79 (67.92) | 5.19 (5.06) | 3.43 (3.55) |
| **6c** | 146-147 | 45 52* | $C_{21}H_{15}Cl_2NO_2S$ 416.32 | 60.58 (60.73) | 3.63 (3.72) | 3.36 (3.47) |
| **7a** | 143-144 | 65 | $C_{21}H_{18}O_5$ 350.36 | 71.99 (71.81) | 5.18 (5.12) | - |
| **7b** | 151-152 | 72 | $C_{23}H_{22}O_7$ 410.41 | 67.31 (67.50) | 5.40 (5.47) | - |
| **7c** | 175-176 | 69 | $C_{21}H_{16}Cl_2O_5$ 419.25 | 60.16 (60.28) | 3.85 (3.90) | - |
| **8a** | 132-133 | 78 | $C_{21}H_{17}NO_3$ 331.36 | 76.12 (76.37) | 5.17 (5.10) | 4.23 (4.33) |
| **8b** | 149-150 | 75 | $C_{23}H_{21}NO_5$ 391.41 | 70.58 (70.77) | 5.41 (5.36) | 3.58 (3.69) |
| **8C** | 135-136 | 71 | $C_{21}H_{15}Cl_2NO_3$ 400.25 | 63.02 (62.90) | 3.78 (3.85) | 3.50 (3.32) |

* Yields obtained in method 2.

Table 2

Physical Properties for Compounds **9-16**

| Comp. | M.P (°C) | Yield (%) | Molecular formula (Molecular weight) | Calcd. (Found) % C | H | N |
|---|---|---|---|---|---|---|
| **9a** | 245-247 | 68 | $C_{19}H_{14}N_2O_2S$ 334.39 | 68.24 (68.10) | 4.22 (4.12) | 8.38 (8.23) |
| **9b** | 238-240 | 64 | $C_{21}H_{18}N_2O_4S$ 394.44 | 63.94 (64.15) | 4.60 (4.51) | 7.10 (7.22) |
| **9c** | 229-231 | 59 | $C_{19}H_{12}Cl_2N_2O_2S$ 403.28 | 56.59 (56.70) | 3.00 (2.93) | 6.94 (6.78) |
| **10a** | 199-200 | 69 | $C_{19}H_{13}NO_3S$ 335.37 | 68.04 (68.26) | 3.91 (3.84) | 4.18 (4.31) |
| **10b** | 211-212 | 61 | $C_{21}H_{17}NO_5S$ 395.43 | 63.79 (63.56) | 4.33 (4.40) | 3.54 (3.63) |
| **10c** | 185-186 | 70 | $C_{19}H_{11}C_{l2}NO_3S$ 404.26 | 56.45 (56.53) | 2.74 (2.70) | 3.46 (3.38) |
| **11a** | 280-282 | 55 | $C_{20}H_{14}N_2O_3S$ 362.42 | 66.28 (66.38) | 3.89 (3.97) | 7.73 (7.63) |
| **11b** | 286-288 | 58 | $C_{22}H_{18}N_2O_5S$ 422.45 | 62.55 (62.75) | 4.29 (4.36) | 6.63 (6.70) |
| **11c** | 274-276 | 51 | $C_{20}H_{12}Cl_2N_2O_3S$ 431.29 | 55.70 (55.54) | 2.80 (2.87) | 6.49 (6.35) |
| **12a** | 282-284 | 60 | $C_{20}H_{14}N_2O_2S_2$ 378.46 | 63.47 (63.55) | 3.73 (3.65) | 7.40 (7.50) |
| **12b** | 277-279 | 59 | $C_{22}H_{18}N_2O_4S_2$ 438.52 | 60.26 (60.14) | 4.14 (4.24) | 6.39 (6.27) |
| **12c** | 268-270 | 57 | $C_{20}H_{12}Cl_2N_2O_2S_2$ 447.36 | 53.70 (53.88) | 2.70 (2.65) | 6.26 (6.37) |
| **13a** | 210-211 | 63 | $C_{19}H_{15}N_3OS$ 333.40 | 68.45 (68.58) | 4.53 (4.44) | 12.60 (12.75) |
| **13b** | 245-247 | 54 | $C_{21}H_{19}N_3O_3S$ 393.46 | 64.10 (64.15) | 4.87 (4.80) | 10.68 (10.80) |
| **13c** | 233-234 | 62 | $C_{19}H_{13}Cl_2N_3OS$ 402.29 | 56.73 (56.59) | 3.26 (3.36) | 10.44 (10.35) |
| **14a** | 182-183 | 65 | $C_{19}H_{14}N_2O_2S$ 334.39 | 68.24 (68.09) | 4.22 (4.17) | 8.38 (8.51) |
| **14b** | 169-170 | 60 | $C_{21}H_{18}N_2O_4S$ 394.44 | 63.94 (63.71) | 4.60 (4.56) | 7.10 (7.23) |
| **14C** | 195-196 | 58 | $C_{19}H_{12}Cl_2N_2O_2S$ 403.28 | 56.59 (56.74) | 3.00 (3.07) | 6.95 (6.83) |
| **15a** | 266-268 | 65 | $C_{20}H_{15}N_3O_2S$ 361.41 | 66.46 (66.65) | 4.18 (4.27) | 11.63 (11.72) |
| **15b** | 272-274 | 69 | $C_{22}H_{19}N_3O_4S$ 421.47 | 62.69 (62.77) | 4.54 (4.59) | 9.97 (9.85) |
| **15c** | 291-293 | 66 | $C_{20}H_{13}Cl_2N_3O_2S$ 430.31 | 55.82 (55.66) | 3.05 (2.98) | 9.77 (9.81) |
| **16a** | 257-259 | 72 | $C_{20}H_{15}N_3OS_2$ 377.48 | 63.64 (63.54) | 4.01 (4.08) | 11.13 (11.28) |
| **16b** | 294-296 | 68 | $C_{22}H_{19}N_3O_3S_2$ 437.53 | 60.39 (60.57) | 4.38 (4.48) | 9.60 (9.49) |
| **16c** | 281-283 | 70 | $C_{20}H_{13}Cl_2N_3OS_2$ 446.37 | 53.81 (53.70) | 2.94 (2.88) | 9.41 (9.58) |

7,10-diene-1,3,5-trione (**11**) and 8,10-diaryl-3-thioxo-9-thia-2,4-diaza-spiro[5,5]undeca-7,10-diene-1,5-dione (**12**) respectively (see Scheme 2). In a similar way the reaction of **6** in the presence of sodium ethoxide furnished 4-amino-7,9-diaryl-8-thia-2,3-diazaspiro[4,5]deca-3,6,9-trien-1-one (**13**), 4-amino-7,9-diaryl-2-oxa-8-thia-3-aza-spiro[4,5]deca-3,6,9-trien-1-one (**14**), 5-amino-3-hydroxy-8,10-diaryl-9-thia-2,4-diazaspiro[5,5]undeca-2,4,7,10-tetraen-1-one (**15**) and 5-amino-3-mercapto-8,10-diaryl-9-thia-2,4-diaza-spiro[5,5]undeca-2,4,7,10-teraen-1-one (**16**) (see Scheme 3 and Table 2). The IR spectra of **9-16** exhibited absorption bands in the region 1495-1510 (C=S) [4], 1655-1725 (*CO*NH), 1745-1770 (*CO*-O), 3300-3440 (OH) and 3100-3310 (CONH, and $NH_2$). The absorption for the SH group generally appears as a weak band around 2550-2600 [5], however this is not observed for our compounds. The $^1H$ NMR spectra of all these compounds showed singlets at 1.41-1.42 (SH), 5.20-5.67 ($C_6$-H and $C_{10}$-H, $C_7$-H and $C_{11}$-H) and 8.88-10.22 ($NH_2$, NH and OH). The $\delta_C$ values obtained in their $^{13}C$ NMR spectra also support the structures (Table 4).

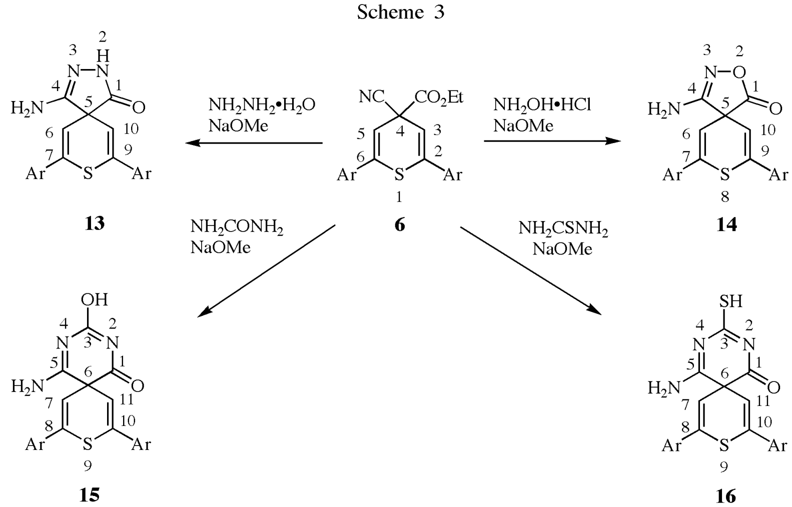
In conclusion, interesting spiro heterocycles were conveniently prepared by a straightforward successfully established method from simple substrates such as phenacyl bromide and active methylene compounds.

Table 3

Spectroscopic Data of Compounds **3-8**

| Compd. | $^1$H NMR δ ($CDCl_3$), ppm | $^{13}$C NMR δ ($CDCl_3$), ppm |
|---|---|---|
| **3a** | 3.82 (s, 6H, $CO_2CH_3$), 5.24 (s, 2H, $C_3$ and $C_5$-H), 7.20-7.74 (m, 10H, ArH), 9.03 (s, 1H, NH Exch. with $D_2O$) | 45.21 ($C_4$), 52.35 ($CO_2CH_3$), 119.11 ($C_3$ and $C_5$), 142.15 ($C_2$ and $C_6$), 173.25 (*C*OOCH$_3$) |
| **3b** | 3.62 (s, 6H, Ar-O$CH_3$), 3.83 (s, 6H, $CO_2CH_3$), 5.29 (s, 2H, $C_3$ and $C_5$-H), 7.19-7.75 (m, 8H, ArH), 9.22 (s, 1H, NH Exch. with $D_2O$) | ______ |
| **3c** | 3.83 (s, 6H, $CO_2CH_3$), 5.22 (s, 2H, $C_3$ and $C_5$-H), 7.22-7.75 (m, 8H, ArH), 9.13 (s, 1H, NH Exch. with $D_2O$) | 45.62 ($C_4$), 52.41 ($CO_2CH_3$), 119.27 ($C_3$ and $C_5$), 142.35 ($C_2$ and $C_6$), 173.28 (*C*OOCH$_3$) |
| **4a** | 1.42 (t, 3H, -$OCH_2CH_3$), 4.36 (q, 2H, -O$CH_2$ $CH_3$), 5.32 (s, 2H, $C_3$ and $C_5$-H), 7.24-7.75 (m, 10H, ArH), 9.20 (s, 1H, NH Exch. with $D_2O$) | 14.21 ($OCH_2CH_3$, 45.23 ($C_4$), 63.55 (-O$CH_2CH_3$), 113.25 (CN), 120.24 ($C_3$ and $C_5$), 142.21 ($C_2$ and $C_6$), 169.48 (*C*OOCH$_2$CH$_3$) |
| **4b** | 1.44 (t, 3H, -$OCH_2CH_3$), 3.57 (s, 6H, Ar-O$CH_3$), 4.35 (q, 2H, -O$CH_2CH_3$), 5.38 (s, 2H, $C_3$ and $C_5$-H), 7.23-7.75 (m, 8H, ArH, 9.06 (s, 1H, NH exch. with $D_2O$) | 14.19 ($OCH_2CH_3$), 45.27 ($C_4$), 51.62 (Ar-O$CH_3$), 63.58 (-O$CH_2CH_3$), 113.54 (CN), 120.54 ($C_3$ and $C_5$), 142.28 ($C_2$ and $C_6$), 169.00 (*C*OOCH$_2$CH$_3$) |
| **4c** | 1.41 (t, 3H, -$OCH_2CH_3$), 4.36 (q, 2H, -O$CH_2$ $CH_3$), 5.33 (s, 2H, $C_3$ and $C_5$-H), 7.24-7.75 (m, 8H, ArH), 9.11 (s, 1H, NH exch. with $D_2O$) | ______ |
| **5a** | 3.78 (s, 6H, $CO_2CH_3$), 5.84 (s, 2H, $C_3$ and $C_5$-H), 7.19-7.75 (m, 10H, ArH) | 45.49 ($C_4$), 52.51 ($CO_2CH_3$), 110.23 ($C_3$ and $C_5$), 145.17 ($C_2$ and $C_6$), 171.29 (*C*OOCH$_3$) |
| **5b** | 3.61 (s, 6H, Ar-O$CH_3$), 3.82 (s, 6H, $CO_2CH_3$), 5.86 (s, 2H, $C_3$ and $C_5$-H), 7.22-7.75 (m, 8H, ArH) | 45.57 ($C_4$), 52.56 ($CO_2CH_3$), 51.72 (Ar-O$CH_3$), 110.77 ($C_3$ and $C_5$),145.61 ($C_2$ and $C_6$), 171.98 (*C*OOCH$_3$) |
| **5c** | 3.79 (s, 6H, $CO_2CH_3$), 5.82 (s, 2H, $C_3$ and $C_5$-H), 7.20-7.75 (m, 8H, ArH) | ______ |
| **6a** | 1.43 (t, 3H, -$OCH_2CH_3$), 4.37 (q, 2H, -O$CH_2$ $CH_3$), 5.77 (s, 2H, $C_3$ and $C_5$-H), 7.21-7.75 (m, 10H, ArH) | 14.68 ($OCH_2CH_3$), 45.67 ($C_4$), 63.65 (-O$CH_2CH_3$), 110.82 ($C_3$ and $C_5$), 113.61 (CN), 151.53 ($C_2$ and $C_6$), 168.89 (*C*OOCH$_2$CH$_3$) |
| **6b** | 1.43 (t, 3H, -$OCH_2CH_3$), 3.62 (s, 6H, Ar-O$CH_3$), 4.38 (q, 2H, -O$CH_2CH_3$), 5.75 (s, 2H, $C_3$ and $C_5$-H), 7.20-7.75 (m, 8H, ArH) | ______ |
| **6c** | 1.41 (t, 3H, -$OCH_2CH_3$), 4.36 (q, 2H, -O$CH_2$ $CH_3$), 5.75 (s, 2H, $C_3$ and $C_5$-H), 7.21-7.76 (m, 8H, ArH) | 14.58 ($OCH_2CH_3$), 45.66 ($C_4$), 63.67 (-O$CH_2CH_3$), 110.81 ($C_3$ and $C_5$), 113.58 (CN), 152.28 ($C_2$ and $C_6$), 168.57 (*C*OOCH$_2$CH$_3$) |
| **7a** | 3.80 (s, 6H, $CO_2CH_3$), 5.76 (s, 2H, $C_3$ and $C_5$-H), 7.25-7.75 (m, 10H, ArH) | 41.52 ($C_4$), 53.21 ($CO_2CH_3$), 93.72 ($C_3$ and $C_5$), 149.98 ($C_2$ and $C_6$), 170.18 (*C*OOCH$_3$) |
| **7b** | 3.62 (s, 6H, Ar-O$CH_3$), 3.83 (s, 6H, $CO_2CH_3$), 5.72 (s, 2H, $C_3$ and $C_5$-H), 7.28-7.75 (m, 8H, ArH) | ______ |
| **7c** | 3.81 (s, 6H, $CO_2CH_3$), 5.75 (s, 2H, $C_3$ and $C_5$-H), 7.29-7.74 (m, 8H, ArH) | 41.95 ($C_4$), 53.26 ($CO_2CH_3$), 91.78 ($C_3$ and $C_5$), 149.00 ($C_2$ and $C_6$), 169.97 (*C*OOCH$_3$) |
| **8a** | 1.40 (t, 3H, -$OCH_2CH_3$), 4.35 (q, 2H, -O$CH_2$ $CH_3$), 5.62 (s, 2H, $C_3$ and $C_5$-H), 7.24-7.77 (m, 10H, ArH) | 14.18 ($OCH_2CH_3$), 41.08 ($C_4$), 63.54 (-O$CH_2CH_3$), 94.05 ($C_3$ and $C_5$), 112.80 (CN), 151.48 ($C_2$ and $C_6$), 167.82 (*C*OOCH$_2$CH$_3$) |
| **8b** | 1.43 (t, 3H, -$OCH_2CH_3$), 3.59 (s, 6H, Ar-O$CH_3$), 4.33 (q, 2H, -O$CH_2CH_3$), 5.65 (s, 2H, $C_3$ and $C_5$-H), 7.22-7.74 (m, 8H, ArH) | ______ |
| **8c** | 1.39 (t, 3H, -$OCH_2CH_3$), 4.38 (q, 2H, -O$CH_2$ $CH_3$), 5.64 (s, 2H, $C_3$ and $C_5$-H), 7.21-7.72 (m, 8H, ArH) | 14.15 (-$OCH_2CH_3$), 41.24 ($C_4$), 63.56 (-O$CH_2CH_3$), 94.90 ($C_3$ and $C_5$), 112.77 (CN), 151.42 ($C_2$ and $C_6$), 168.11 (*C*OOCH$_2$CH$_3$) |

Scheme 3




Ar a) $C_6H_5$, b) 4-OMe$C_6H_4$, c) 4-Cl$C_6H_4$

Table 4

Spectroscopic Data of Compounds **9-16**

| Compd | $^1$H NMR δ (DMSO-$d_6$), ppm | $^{13}$C NMR δ (DMSO-$d_6$), ppm |
|---|---|---|
| **9a** | 5.25 (s, 2H, $C_6$ and $C_{10}$-H), 7.25-7.76 (m, 10H, ArH), 9.09 (s, 2H, NH Exch. with $D_2O$) | 45.18 ($C_5$), 117.22 ($C_6$ and $C_{10}$), 145.20 ($C_7$ and $C_9$), 169.48 ($C_1$ and $C_4$) |
| **9b** | 3.62 (s, 6H, Ar-O*CH*$_3$), 5.23 (s, 2H, $C_6$ and $C_{10}$-H), 7.22-7.77 (m, 8H, ArH), 9.17 (s, 2H, NH Exch. with $D_2O$) | 45.01 ($C_5$), 51.68 (Ar-O$CH_3$), 117.29 ($C_6$ and $C_{10}$), 145.25 ($C_7$ and $C_9$), 169.29 ($C_1$ and $C_4$) |
| **9c** | 5.20 (s, 2H, $C_6$ and $C_{10}$-H), 7.21-7.75 (m, 8H, ArH), 9.25 (s, 2H, NH Exch. with $D_2O$) | ——— |
| **10a** | 5.27 (s, 2H, $C_6$ and $C_{10}$-H), 7.22-7.76 (m, 10H, ArH), 10.15 (s, 1H, NH Exch. with $D_2O$) | 46.22 ($C_5$), 117.39 ($C_6$ and $C_{10}$), 146.21 ($C_7$ and $C_9$), 169.23, 171.45 ($C_1$ and $C_4$) |
| **10b** | 3.60 (s, 6H, Ar-O*CH*$_3$), 5.31 (s, 2H, $C_6$ and $C_{10}$-H), 7.28-7.87 (m, 8H, ArH), 10.18 (s, 1H, NH Exch. with $D_2O$) | 46.84 ($C_5$), 51.72 (Ar-O$CH_3$), 117.98 ($C_6$ and $C_{10}$), 146.54 ($C_7$ and $C_9$), 169.02, 171.51 ($C_1$ and $C_4$) |
| **10c** | 5.52 (s, 2H, $C_6$ and $C_{10}$-H), 7.21-7.76 (m, 8H, ArH), 10.22 (s, 1H, NH Exch. with $D_2O$) | ——— |
| **11a** | 5.61 (s, 2H, $C_7$ and $C_{11}$-H), 7.38-7.76 (m, 10H, ArH), 9.01 (s, 2H, NH Exch. with $D_2O$) | 45.28 ($C_6$), 117.49 ($C_7$ and $C_{11}$), 146.99 ($C_8$ and $C_{10}$), 159.82 ($C_3$) 171.97 ($C_1$ and $C_5$) |
| **11b** | 3.60 (s, 6H, Ar-O*CH*$_3$), 5.63 (s, 2H, $C_7$ and $C_{11}$-H), 7.22-7.81 (m, 8H, ArH), 8.88 (s, 2H, NH Exch. with $D_2O$) | ——— |
| **11c** | 5.61 (s, 2H, $C_7$ and $C_{11}$-H), 7.21-7.75 (m, 8H, ArH), 8.89 (s, 2H, NH Exch. with $D_2O$) | ——— |
| **12a** | 5.53 (s, 2H, $C_7$ and $C_{11}$-H), 7.22-7.76 (m, 10H, ArH), 9.12 (s, 2H, NH Exch. with $D_2O$) | 45.50 ($C_6$), 118.04 ($C_7$ and $C_{11}$), 147.02 ($C_8$ and $C_{10}$), 159.87 ($C_3$) 171.64 ($C_1$ and $C_5$) |
| **12b** | 3.62 (s, 6H, Ar-O*CH*$_3$), 5.55 (s, 2H, $C_7$ and $C_{11}$-H), 7.21-7.77 (m, 8H, ArH), 9.15 (s, 2H, NH Exch. with $D_2O$) | ——— |
| **12c** | 5.67 (s, 2H, $C_7$ and $C_{11}$-H), 7.20-7.76 (m, 8H, ArH), 9.21 (s, 2H, NH Exch. with $D_2O$) | 45.42 ($C_6$), 116.93 ($C_7$ and $C_{11}$), 147.52 ($C_8$ and $C_{10}$), 159.81 ($C_3$) 171.59 ($C_1$ and $C_5$) |
| **13a** | 5.49 (s, 2H, $C_6$ and $C_{10}$-H), 7.20-7.75 (m, 10H, ArH), 9.32-9.36 (bs, 3H, $NH_2$, NH Exch.with $D_2O$) | 43.98 ($C_5$), 119.14 ($C_6$ and $C_{10}$), 142.92 ($C_7$ and $C_9$), 165.02 ($C_4$) 170.21 ($C_1$) |
| **13b** | 3.61 (s, 6H, Ar-O*CH*$_3$), 5.44 (s, 2H, $C_6$ and $C_{10}$-H), 7.21-7.75 (m, 8H, ArH), 9.41-9.45 (bs, 3H, $NH_2$, NH Exch. with $D_2O$) | ——— |
| **13c** | 5.43 (s, 2H, $C_6$ and $C_{10}$-H), 7.22-7.76 (m, 8H, ArH), 9.40-9.43 (bs, 3H, $NH_2$, NH Exch. with $D_2O$) | 44.26 ($C_5$), 118.91 ($C_6$ and $C_{10}$), 143.76 ($C_7$ and $C_9$), 164.12 ($C_4$) 170.42 ($C_1$) |
| **14a** | 5.48 (s, 2H, $C_6$ and $C_{10}$-H), 7.24-7.76 (m, 10H, ArH), 9.81 (s, 2H, $NH_2$ Exch. with $D_2O$) | 45.55 ($C_5$), 119.12 ($C_6$ and $C_{10}$), 143.28 ($C_7$ and $C_9$), 165.49 ($C_4$) 173.21 ($C_1$) |
| **14b** | 3.62 (s, 6H, Ar-O*CH*$_3$), 5.47 (s, 2H, $C_6$ and $C_{10}$-H), 7.25-7.75 (m, 8H, ArH), 9.83 (s, 2H, $NH_2$ Exch. with $D_2O$) | ——— |
| **14c** | 5.45 (s, 2H, $C_6$ and $C_{10}$-H), 7.23-7.77 (m, 8H, ArH), 9.84 (s, 2H, $NH_2$ Exch. with $D_2O$) | 45.51 ($C_6$), 119.92 ($C_6$ and $C_{10}$), 143.91 ($C_7$ and $C_9$), 164.91 ($C_4$) 172.82 ($C_1$) |
| **15a** | 5.44 (s, 2H, $C_7$ and $C_{11}$-H), 7.21-7.76 (m, 10H, ArH), 9.17 (s, 1H, OH Exch. with $D_2O$), 9.89 (s, 2H, $NH_2$ Exch. with $D_2O$) | 43.23 ($C_6$), 117.62 ($C_7$ and $C_{11}$), 143.01 ($C_8$ and $C_{10}$), 162.34 ($C_3$) 178.45 ($C_1$), 186.77 ($C_5$) |
| **15b** | 3.58 (s, 6H, Ar-O*CH*$_3$), 5.46 (s, 2H, $C_7$ and $C_{11}$-H), 7.21-7.75 (m, 8H, ArH), 9.16 (s, 1H, OH Exch. with $D_2O$), 9.80 (s, 2H, $NH_2$ Exch. with $D_2O$) | 43.27 ($C_6$), 51.71 (Ar-O$CH_3$) 117.31 ($C_7$ and $C_{11}$), 143.24 ($C_8$ and $C_{10}$), 162.21 ($C_3$) 178.92 ($C_1$), 186.22 ($C_5$) |
| **15c** | 5.48 (s, 2H, $C_7$ and $C_{11}$-H), 7.20-7.76 (m, 8H, ArH), 9.19 (s, 1H, OH Exch. with $D_2O$), 9.81 (s, 2H, $NH_2$ Exch. with $D_2O$) | ——— |
| **16a** | 1.43 (s, 1H, SH Exch.. with $D_2O$), 5.47 (s, 2H, $C_7$ and $C_{11}$-H), 7.21-7.77 (m, 10H, ArH), 9.62 (s, 2H, $NH_2$ Exch. with $D_2O$) | 41.49 ($C_6$), 117.63 ($C_7$ and $C_{11}$), 144.79 ($C_8$ and $C_{10}$), 162.91 ($C_3$) 176.76 ($C_1$), 179.96 ($C_5$) |
| **16b** | 1.45 (s, 1H, SH Exch. Exch. with $D_2O$), 3.60 (s, 6H, Ar-O*CH*$_3$), 5.49 (s, 2H, $C_7$ and $C_{11}$-H), 7.22-7.75 (m, 8H, ArH), 9.60 (s, 2H, $NH_2$ Exch. with $D_2O$) | 41.12 ($C_6$), 51.69 (Ar-O$CH_3$) 116.82 ($C_7$ and $C_{11}$), 145.31 ($C_8$ and $C_{10}$), 163.54 ($C_3$) 176.93 ($C_1$), 180.54 ($C_5$) |
| **16c** | 1.41 (s, 1H, SH Exch. with $D_2O$), 5.48 (s, 2H, $C_7$ and $C_{11}$-H), 7.20-7.75 (m, 8H, ArH), 9.64 (s, 2H, $NH_2$ Exch. with $D_2O$) | ——— |

## EXPERIMENTAL

Melting points were determined on Mel-Temp apparatus and were uncorrected. The IR spectra were recorded on Perkin-Elmer 1600 FT-IR spectrometer using KBr disc. The wave numbers were in $cm^{-1}$. NMR spectra were recorded on a Bruker spectrospin 300 MHz spectrometer with TMS as an internal standard. The chemical shifts were measured in ppm. Purity of the compounds were checked by TLC using silica gel `G' (BDH) and hexane-ethyl acetate as eluents.

2,6-Diaryl-4,4-dimethoxycarbonyl-1,4-dihydropyridine (**3**) or 2,6-diaryl-4-cyano-4-ethoxy- carbonyl-1,4-dihydropyridine (**4**).

A mixture of 10 mmoles of **1** or **2** and 1.5 g of ammonium acetate in 20 ml of acetic acid was refluxed for 2 hours. The reaction mixture was cooled and poured onto crushed ice. The products obtained were recrystallized from methanol to give **3** or **4** (Table 1).

2,6-Diaryl-4,4-dimethoxycarbonyl-4*H*-pyran (**7**) or 2,6-Diaryl-4-cyano-4-ethoxycarbonyl-4*H*-pyran (**8**).

Compounds **1** or **2** (10 mmoles) were dissolved in 30 ml of dry benzene. To this 2 g of phosphorus pentoxide was added and refluxed for 8-10 hours using a Dean-Stark apparatus. The reaction mixture was filtered, washed with water, brine and dried (anhydrous $Na_2SO_4$). The solvent was evaporated *in vacuo*, and the resultant products were recrystallized from ethanol to furnished **7** or **8** (Table 1).

2,6-Diaryl-4,4-dimethoxycarbonyl-4*H*-thiopyran (**5**) or 2,6-diaryl-4-cyano-4-ethoxycarbonyl-4*H*-thiopyran (**6**).

Method 1.

To a solution of 10 mmoles of **1** or **2** in 25 ml of xylene, 15 mmoles of phosphorus pentasulfide was added and refluxed for 10 hours at 130-140 °C. The cooled contents were filtered to remove excess phosphorus pentasulfide. The solvent was removed under reduced pressure. The residue was recrystallized from ethanol to afford **5** or **6** (Table 1).

Method 2: Conversion of **7** or **8** to **5** or **6**.

A solution of 5 mmoles of **7** or **8** in 20 m1 of xylene and 10 mmoles of phosphorus pentasulfide were refluxed for 3 hours and worked up as described above to give **5** or **6** (Table 1).

7,9-Diaryl-8-thia-2,3-diazaspiro[4,5]deca-6,9-diene-1,4-dione (**9**), 7,9-diaryl-2-oxa-8-thia-3-azaspiro[4,5]deca-6,9-diene-1,4-dione (**10**), 8,10-diaryl-9-thia-2,4-diazaspiro[5,5]undeca-7,10-diene-1,3,5-trione (**11**), 8,10-diaryl-3-thioxo-9-thia-2,4-diazaspiro[5,5]undeca-7,10-diene-1,5-dione (**12**).

A mixture of 10 mmoles of **5**, 15 mmoles of 80% hydrazine hydrate or 10 mmoles of either hydroxylamine hydrochloride, urea or thiourea as appropriate (Scheme 2) in 20 ml of methanol and 5 ml of 10% sodium methoxide was refluxed for 5-6 hours. The solution was cooled and poured onto crushed ice containing hydrochloric acid. The solid obtained was recrystallized from methanol to give **9-12** (Table 2).

4-Amino-7,9-diaryl-8-thia-2,3-diazaspiro[4,5]deca-3,6,9-trien-1-one (**13**), 4-amino-7,9-diaryl-2-oxa-8-thia-3-azaspiro[4,5]deca-3,6,9-trien-1-one (**14**), 5-amino-3-hydroxy-8,10-diaryl-9-thia-2,4-diazaspiro[5,5]undeca-2,4,7,10-tetraen-1-one (**15**) and 5-amino-3-mercapto-8,10-diaryl-9-thia-2,4-diazaspiro[5,5]undeca-2,4,7,10-tetraen-1-one (**16**).

To a solution of 10 mmoles of **6** in 20 ml of ethanol, 15 mmoles of hydrazine hydrate or 10 mmoles of either hydroxylamine hydrochloride, urea or thiourea as appropriate (Scheme 3), 5 ml of 10% sodium ethoxide were added and refluxed for 6-8 hours, The cooled reaction mixture was poured onto crushed ice containing acetic acid. The solid separated was recrystallized from methanol to give **13-16** (Table 2).

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