



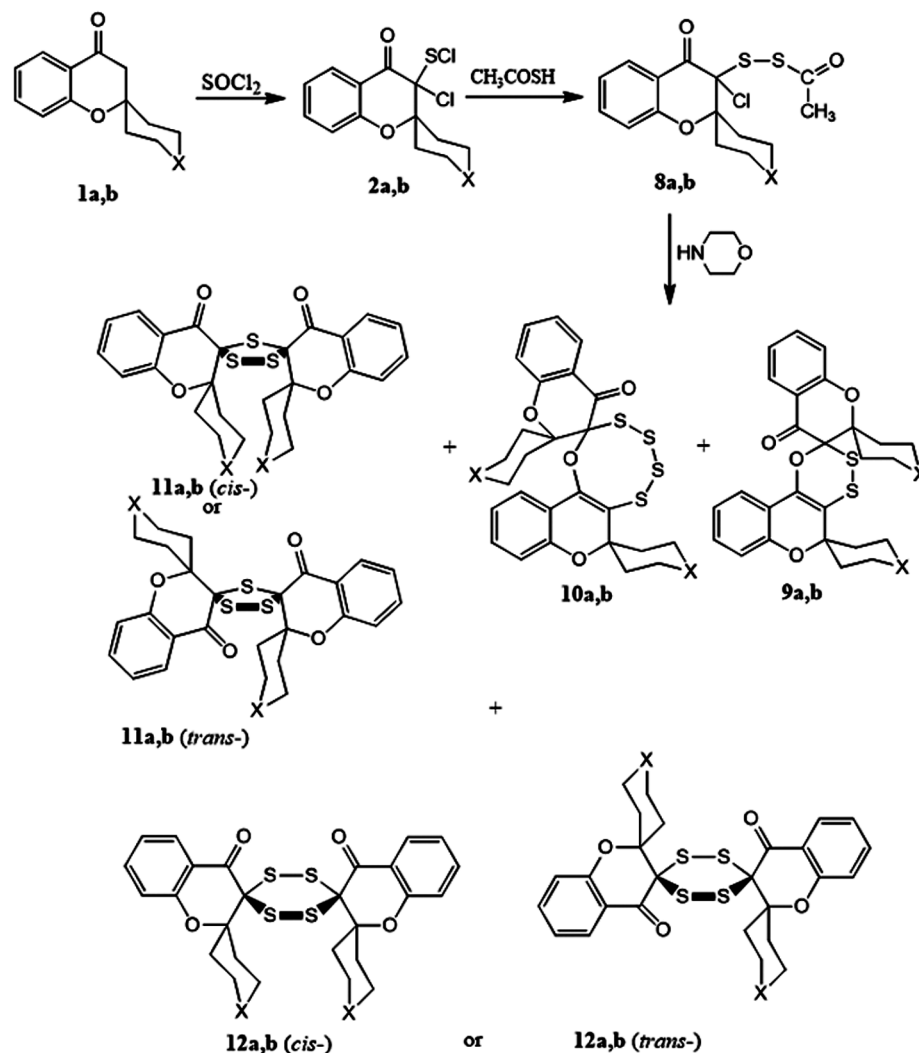




hydrazino-2-tetrahydro(pyrane orthiopyrane) chroman-4-ones **5a,b** according to Scheme 1. The IR spectra of these formed compounds showed a characteristic absorption bands at  $\nu$  3265 and (3167-3150)  $\text{cm}^{-1}$ , at  $\nu$  3269 and (3168-3154)  $\text{cm}^{-1}$ , respectively corresponding to the amino groups NH &  $\text{NH}_2$ , respectively. The  $^1\text{H}$  NMR spectra showed the NH group as singlet at  $\delta$  6.12 ppm of compound **5a** and at  $\delta$  6.14 ppm of compound **5b** in addition to the other protons of these compounds. 5''-mercapto-2,3,5,6-tetrahydro-5''H-dispiro[pyran/thiapyran-4,2'-chromane-3',2''-[1,3,4] thiadiazol]-4'-one **6a,b** were furnished from the reaction of 3-hydrazino-2-tetrahydro(pyrane or thiapyran) chroman-4-ones **5a,b** with carbon disulphide in ethanolic potassium hydroxide (Scheme 1). The desired products were characterized by physical and spectral data. Thus, IR spectra of compounds **6a,b** showed a characteristic absorption band at  $\nu$  1624  $\text{cm}^{-1}$ , at  $\nu$  1630  $\text{cm}^{-1}$  respectively which corresponding to the amide group (N=N). The  $^1\text{H}$  NMR spectra of compounds **6a,b** showed the singlet signal at  $\delta$  14.01 ppm and at  $\delta$  12.10 ppm, respectively corresponding to the SH group in addition to the protons of these compounds.

3-Hydrazino-2-tetrahydro(pyrane orthiapyran)-chroman-4-ones **5a,b** also, reacted with acetylacetone to yield 3'-(3'',6''-dimethylpyridazin-1''(2H)-yl)-2,3,5,6-tetrahydrospiro[chromane-2',4-pyran/thiapyran]-4'-one **7a,b** (Scheme 1), which confirmed *via* IR,  $^1\text{H}$  NMR, and MS spectra. Whereas, IR of compound **7a** showed a characteristic absorption band at  $\nu$  3168  $\text{cm}^{-1}$ (NH), 1689  $\text{cm}^{-1}$ (C=O). and of compound **7b** showed at  $\nu$  3165  $\text{cm}^{-1}$ (NH), 1697  $\text{cm}^{-1}$ (C=O). The  $^1\text{H}$ -NMR spectrum of compound **7a** showed the singlet signals, at  $\delta$  1.85 and at  $\delta$  = 2.01 ppm for the 2  $\text{CH}_3$  groups, 4.60 (s, 1H, 3'-CH), 4.98 (m, 2H, 4''-CH + 5''-CH), 9.18 ppm (br s, 1H, NH). in addition to the protons of the compound. While the  $^1\text{H}$ -NMR spectrum of compound **7b** showed the singlet signals, at  $\delta$  1.77, 1.95 (s, 2H, 2  $\text{CH}_3$ ), 4.62 (s, 1H, 3'-CH), 4.80 (m, 2H, 4''-CH + 5''-CH), 9.20 ppm (br s, 1H, NH) besides the other protons of the compound.

The compounds  $\alpha$ -chlorosulfonyl chloride **2a,b** were treated with thioacetic acid in  $\text{CCl}_4$  at 50  $^\circ\text{C}$  to give  $\alpha$ -chloroalkyl disulfides **8a,b** according to Scheme 2, and the formed compounds were confirmed by spectral data (IR,  $^1\text{H}$  NMR, MS). Where, IR spectrum of compound **8a** showed a

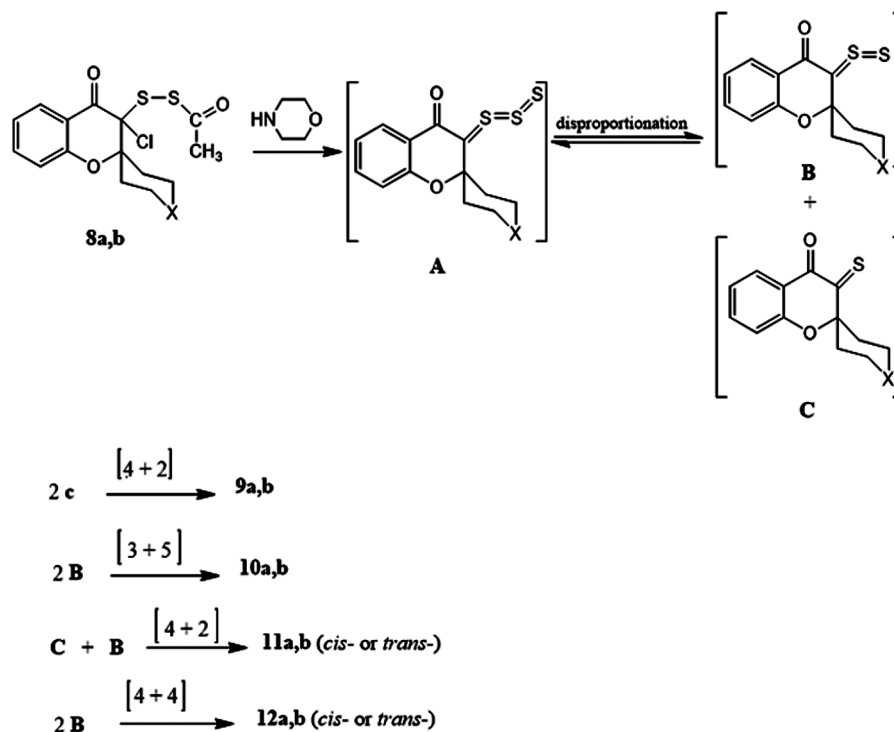


Scheme 2 — Synthesis of compounds 8-12

characteristic absorption band at  $\nu 1708\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ),  $1696\text{ cm}^{-1}$  ( $\text{CO}-\text{CH}_3$ ) and of compound **8b** showed at  $\nu 1710\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ),  $1698\text{ cm}^{-1}$  ( $\text{CO}-\text{CH}_3$ ). The  $^1\text{H-NMR}$  spectra showed a characteristic singlet signal at  $\delta 2.48$  and  $\delta 2.40$  ppm corresponding to the  $\text{CO}-\text{CH}_3$  group of compound **8a** and **8b**, respectively.

However,  $\alpha$ -chloroalkyl disulfides **8a,b** were treated with morpholin in ether at  $50^\circ\text{C}$ , according to reported procedure,<sup>35,36</sup> to afford four components: 2,2''',3,3''',5,5''',6,6'''-octahydrotrispiro[pyran-4,2'-chromane-3',2''-[1,3,4]oxadithiino[5,6-c]chromene-5'',4'''-pyran]-4'-one (**9a,b**) (as known compounds)<sup>22</sup>, 2,2''',3,3''',5,5''',6,6'''-octahydrotrispiro[pyran-4,2'-chromane-3',2''-[1,3,4,5,6]oxatetrathiocino[7,8-c]chromene-7'',4'''-pyran]-4'-one (**10a,b**), cis- and trans-(3'R,5''S)(3'S,5''R)-2,2''',3,3''',5,5''',6,6'''-octahydr

otetraspiro[pyran-4,2'-chromane-3',3''-[1,2,4]trithiane-5'',3'''-chromane-2'',4'''-pyran]-4',4'''-dione (**11a,b**), and cis- and trans-2,2''',3,3''',5,5''',6,6'''-octahydrotrispiro[pyran-4,2'-chromane-3',3''-[1,2,4,5]tetrathiane-6'',3'''-chromane-2'',4'''-pyran]-4',4'''-dione (**12a,b**) which are separated by column chromatography (silica gel, Merck 90, particle size 0.063-0.200 mm, ether-hexane 1:5 as an eluent) (Scheme 2). IR spectrum of compound **10a** showed a characteristic absorption band at  $\nu 1694\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ) and of compound **10b** showed at  $\nu 1694\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ). The  $^1\text{H-NMR}$  spectra showed the signals corresponding to the protons of the compounds **10a** and **10b**, whereas the MS spectra of compounds **10a,b** shows the molecular ion peak at  $m/z$  560, 592, respectively. IR spectra of compounds **11a,b** showed a characteristic absorption



Scheme 3 — Synthesis of compounds 9-12

band at  $\nu 1694, 1690 \text{ cm}^{-1}$  (2 C=O). The  $^1\text{H-NMR}$  spectra showed the signals corresponding to the protons of the compounds **11a** and **11b**, whereas the MS spectra of compounds **11a,b** shows the molecular ion peak at  $m/z$  528, 560, respectively. However the compounds **12a,b** were confirmed by spectral data (IR,  $^1\text{H}$  NMR, MS). Where, IR spectra showed a characteristic absorption band at  $\nu 1697, 1693 \text{ cm}^{-1}$  (2 C=O), The  $^1\text{H}$  NMR spectra showed the signals corresponding to the protons of the compounds **12a** and **12b**, whereas the MS spectra of compounds **12a,b** shows the molecular ion peak at  $m/z$  560, 592, respectively. The formation of the four compounds **9-12** could be explained via Scheme 3.

### Conclusion

3-Chlorochromanone derivatives were treated with hydrazine hydrate afforded 3-hydrazino-2-tetrahydro(pyran or thiopyran)chroman-4-ones which reacted with carbon disulfide and with acetylacetone to give 5'-thiolo-2-tetrahydro(pyran or thiopyran)-spiro[chroman-3,2'-[1,3,4]-thiadiazole]-4-one and 3', 5'-dimethyl-2-tetrahydro(pyran or thiopyran) spiro[chroman-3,2'-piperazine]-4-one, respectively.  $\alpha$ -Chlorosulfonyl chlorides were treated with thioacetic acid to form  $\alpha$ -chloroalkyl disulfides, the latter

compounds were reacted with morpholine to yield a mixture of 1,3,4-oxadithiins, 1,3,4,5,6-oxatetrathiocins, 1,2,4-trithiolanes (*cis*- and *trans*-), 1,2,4,5-tetrathiiins (*cis*- and *trans*-), which are separated via column chromatography.

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