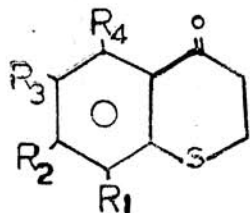


## SYNTHESIS OF SOME THIOCHROMANONES

IN continuation of our previous paper on the synthesis of  $\alpha$ -pyronochromanones, the present work describes the S-cyanoethylation of the different thiocresols leading to the synthesis of thiochromanones.



- I,  $R_1 = \text{CH}_3$ ;  $R_2 = R_3 = R_4 = \text{H}$ .  
 II,  $R_4 = \text{CH}_3$ ;  $R_1 = R_2 = R_3 = \text{H}$ .  
 III,  $R_2 = \text{CH}_3$ ;  $R_1 = R_3 = R_4 = \text{H}$ .  
 IV,  $R_3 = \text{CH}_3$ ;  $R_1 = R_2 = R_4 = \text{H}$ .

The reaction of *o*-thiocresol with acrylonitrile in the presence of aq. NaOH (10%) in boiling dioxane for 15 hrs. yielded the corresponding mercaptopropionitrile<sup>1</sup> as a light yellow oil (b.p. 177°/18 mm) which was hydrolysed by heating with conc. HCl (1 hour) to the propionic acid, crystallised from benzene-petroleum ether in colourless needles, m.p. 93–95° (Found: C, 60.8; H, 6.1%;  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}$  requires: C, 61.2; H, 6.1%). Cyclisation of the above acid on heating with conc.  $\text{H}_2\text{SO}_4$  on a water bath for about 10 minutes afforded 8-methyl-thiochromanone (I) crystallised from benzene-petroleum ether in colourless needles, m.p. 65–70° (Found: C, 67.3; H, 5.9%.  $\text{C}_{10}\text{H}_{10}\text{OS}$  requires: C, 67.4; H, 5.6%). The NMR ( $\text{CCl}_4$ ) spectrum was fully consistent with its structure and showed signals at  $\delta$  2.3 (3 H, s,  $-\text{CH}_3$  at  $\text{C}_8$ );  $\delta$  3.5 (4 H, m,  $-\text{CH}_2$  at  $\text{C}_2$  and  $\text{CH}_2$  at  $\text{C}_3$ );  $\delta$  7.1 (2 H, m, at  $\text{C}_6$  and  $\text{C}_7$ );  $\delta$  7.95 (1 H, d, at  $\text{C}_5$ ,  $J = 2$  Hz and 6 Hz). The 2, 4-DNP from (I) had m.p. 238–39° (Found: N, 15.5%;  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_4\text{S}$  requires: N, 15.6%).

The mercaptonitrile from *m*-thiocresol by cyanoethylation under the above conditions was a yellow oil (b.p. 175–78°/18 mm) and gave the mercapto acid as colourless needles from benzene-petroleum ether, m.p. 68–70° (Found: C, 61.1; H, 6.4%.  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}$  requires: C, 61.2; H, 6.1%). Cyclisation of the latter acid with conc.  $\text{H}_2\text{SO}_4$  yielded a reddish brown oil which was chromatographed over neutral alumina. The fraction eluted with petrol ether was a yellow oil (b.p. 124°/2.5 mm) which was assigned the structure as 5-methyl-thiochromanone (II) on the basis of its NMR data

(Found: C, 67.3; H, 5.6%.  $\text{C}_{10}\text{H}_{10}\text{OS}$  requires: C, 67.4; H, 5.6%). NMR ( $\text{CCl}_4$ ):  $\delta$  2.55 (3 H, s,  $-\text{CH}_3$ );  $\delta$  3.0 (4 H, m,  $-\text{CH}_2$  at  $\text{C}_2$  and  $-\text{CH}_2$  at  $\text{C}_3$ ) at  $\delta$  6.95 (3 H, m, at  $\text{C}_6$ ,  $\text{C}_7$  and  $\text{C}_8$ ) 2, 4-DNP of II, m.p. 206° (Found: N, 15.4%.  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{SN}_4$  requires: N, 15.6%). The fraction eluted with petrol ether-benzene (1:4) was a reddish oil, b.p. 146°/2.5 mm (Found: C, 67.1; H, 5.4%.  $\text{C}_{10}\text{H}_{10}\text{OS}$  requires: C, 67.4; H, 5.6%). Its 2, 4-DNP had m.p. 223° (Found: N, 15.7%.  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{SN}_4$  requires: N, 15.6%). Its structure as 7-methyl-thiochromanone (III) was in complete agreement with its NMR spectrum ( $\text{CCl}_4$ ):  $\delta$  2.35 (3 H, s,  $-\text{CH}_3$ );  $\delta$  3.0 (4 H, m,  $-\text{CH}_2$  at  $\text{C}_2$  and  $-\text{CH}_2$  at  $\text{C}_3$ );  $\delta$  6.90 (1 H, d, at  $\text{C}_8$ ,  $J = 2$  Hz);  $\delta$  6.98 (1 H, dd, at  $\text{C}_6$ ,  $J = 8$  Hz and 2 Hz);  $\delta$  7.9 (1 H, d, at  $\text{C}_5$ ,  $J = 8$  Hz).

By the cyanoethylation of *p*-thiocresol, the required propionitrile was obtained as a yellow oil<sup>1</sup> (b.p. 174°/18 mm) which was easily hydrolysed with HCl to give the corresponding acid as colourless needles, m.p. 70° from benzene-petrol ether. On cyclisation, the acid afforded 6-methyl-thiochromanone (IV) as colourless needles, m.p. 41°<sup>2</sup>, 2, 4-DNP, m.p. 285–86° (Found: N, 15.8%.  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_4\text{S}$  requires: N, 15.6%). NMR ( $\text{CDCl}_3$ ) of IV:  $\delta$  2.3 (3 H, s,  $-\text{CH}_3$ );  $\delta$  2.9–3.1 (4 H, m, methylene protons at  $\text{C}_2$  and  $\text{C}_3$ );  $\delta$  7.15 (2 H, s, at  $\text{C}_7$  and  $\text{C}_8$ );  $\delta$  7.9 (1 H, s, at  $\text{C}_5$ ).

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1. Hurd, C. D. and Gerahbein, L. L., *J. Am. Chem. Soc.*, 1947, 69, 2328.
2. Arndt, F., Flemming, W., Scholz, E. and Lowenson, V., *Ber.*, 1923, 56B, 1279.