A new method for synthesis of 6-aryl-2*H*-thiopyran-2-thiones

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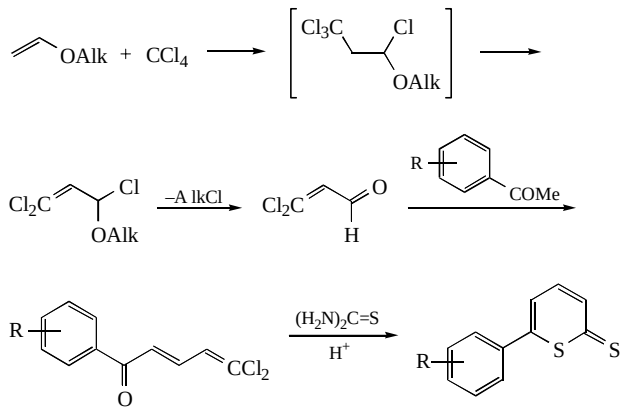
A simple and convenient method for the synthesis of 6-aryl-2*H*-thiopyran-2-thiones by the interaction of 1-aryl-5,5-dichloropenta-2,4-dienones with thiourea in acidic media is reported.

Thiopyranthiones **1** can be used as intermediates for the synthesis of polynitrogen-containing heterocyclic systems.[1] Several methods for the preparation of 2*H*-thiopyran-2-thiones are described in the literature but most of them involve the use of difficultly available or toxic starting materials. Thus, a method for the preparation of 6-substituted or 3,6-disubstituted 2*H*-thiopyran-2-thiones from aryl aminovinyl thioketones and ketenes followed by treatment of the resulting thiopyrans with phosphorus pentasulfide has been reported.[2] 3,5-Disubstituted 2*H*-thiopyran-2-thiones have been obtained by reaction of enamines bearing aliphatic or aromatic substituents with carbon disulfide.[3] 3-Acyl- or 3,6-diaryl-2*H*-thiopyran-2-thiones have been obtained by the action of dithiol-1,2-ylium salts on methyl 2-aroyl (or 2-acyl) dithioacetates.[4]



2a–f **1a–f**

a R = H **d** R = *p*-OMe
b R = *p*-Cl **e** R = *m*-Br
c R = *p*-Me **f** R = 3,4-OCH_2O

In this paper, we report a simple and convenient method for the synthesis of 6-aryl-2*H*-thiopyran-2-thiones **1** by the interaction of 1-aryl-5,5-dichloropenta-2,4-dienones **2**† with thiourea in acidic media.‡ This method facilitates significantly the synthesis of the target compounds as the starting compounds have been obtained from readily available methyl aryl ketones and dichloroacrolein (or its monochloroacetals). The latter are formed by the radical addition of CCl_4 to vinyl ethers.[5-6]

Compounds **1** are formed on heating compounds **2** and thiourea in ethanol in the presence of hydrochloric acid. 5,6-Dihydro-2*H*-benzo[*h*]thiochromen-2-thione **3** was prepared in the same manner from 2-(3,3-dichloro-2-propenylidene)-1,2,3,4-tetrahydronaphthalen-1-one. The structures of the obtained compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis data.§ The probable pathway of the reaction involves the replacement of one or two chlorine atoms of the dichlorovinyl moiety giving mercapto derivatives or isothiuronium salts. Next, cyclization proceeds in a similar manner as in the formation of 6-aryl-2*H*-pyran-2-ones from compounds **2**.[6]

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† *1-(3,4-Methylenedioxyphenyl)-5,5-dichloropenta-2,4-dienone* **2f** was obtained as described previously;[5] mp 134–135 °C, yield 56%. Found (%): C, 53.11; H, 2.83; Cl, 26.00. Calc. for $C_{12}H_8Cl_2O_3$ (%): C, 53.17; H, 2.97; Cl, 26.15.

‡ *General procedure for the preparation of 6-aryl-2H-thiopyrane-2-thiones* **1**. A mixture of compound **2** (4 mmol), thiourea (10–20 mmol) and conc. HCl (0.4 ml) in 10 ml of ethanol was refluxed for 6–7 h. The resulting solution was kept overnight and the residue was filtered off and recrystallised from ethanol. In some cases, the mother liquor was evaporated, and the residue was chromatographed (silica gel; eluent: ethyl acetate–hexane, 1:1).

§ The NMR spectra were recorded on Bruker WM-250 and Bruker AM-300 instruments in [$^2H_6$]DMSO solutions.

1a: mp 66–67 °C (lit.,[2] mp 66–68 °C), yield 27%. ^{1}H NMR, δ: 7.5 (m, 5H), 7.7 (m, 3H).

1b: mp 111–112 °C (lit.,[2] mp 110–111 °C), yield 35%. ^{1}H NMR, δ: 7.1 (d, 2H), 7.42 (dd, 2H), 7.62 (dd, 3H). ^{13}C NMR, δ: 121.6 [C(3)], 128 ($C_{Ar\text{-}meta}$), 129.3 ($C_{Ar\text{-}ortho}$), 133 ($C_{Ar\text{-}ipso}$), 135.6 [C(4)], 135.7 ($C_{Ar\text{-}para}$), 136.5 [C(5)], 154.8 [C(6)], 203.9 [C(2), C=S]. MS, *m*/*z*: 238 [M$^+$].

1c: mp 78–79 °C (lit.,[2] mp 79–81 °C), yield 27%. ^{1}H NMR, δ: 2.4 (s, 3H, Me), 7.17 (dd, 1H), 7.27 (dd, 3H), 7.45 (dd, 3H).

1d: mp 68–69 °C (lit.,[2] mp 67–68 °C), yield 32%. ^{1}H NMR, δ: 3.8 (s, 3H, OMe), 7.1 (d, 2H), 7.45 (m, 2H), 7.6 (d, 1H), 7.75 (d, 2H). ^{13}C NMR, δ: 114.1 ($C_{Ar\text{-}meta}$), 120.3 [C(3)], 127 ($C_{Ar\text{-}ipso}$), 128.1 ($C_{Ar\text{-}ortho}$), 135.7 [C(4)], 136.5 [C(5)], 157.2 [C(6)], 161.7 ($C_{Ar\text{-}para}$), 203.6 [C(2), C=S]. MS, *m*/*z*: 234 [M$^+$].

1e: mp 106–108 °C, yield 12%. ^{1}H NMR, δ: 7.5 (m, 3H), 7.75 (m, 3H), 7.95 (s, 1H). MS, *m*/*z*: 282, 284 [M$^+$].

1f: mp 185–186 °C, yield 38%. ^{1}H NMR, δ: 6.1 (s, 2H, CH_2), 7.05 (d, 1H), 7.2 (d, 1H), 7.3 (s, 1H), 7.4 (dd, 2H), 7.6 (d, 1H). MS, *m*/*z*: 248 [M$^+$].

3: mp 110–111 °C, yield 71%. ^{1}H NMR, δ: 2.85 (m, 4H), 7.4 (m, 5H), 7.65 (d, 1H). Found (%): C, 67.70; H, 4.39; S, 27.28. Calc. for $C_{13}H_{10}S_2$ (%): C, 67.79; H, 4.38; S, 27.84.