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I-1604-m1

Supplementary Material:

Synthesis procedures, ^{1}H NMR, mass spectral and/or analytical data for **4**, **6** and **7**.

Reaction procedure for **4**.

A solution of **5** (0.4 g, 1.22 mmol) in acetic anhydride (30 ml) was added to a solution of 1,3 diphenyl thiobarbituric acid (0.54g, 1.82 mmol) in acetic anhydride (5 ml). The resulting solution immediately turned green/blue and was refluxed for 15 minutes. The acetic anhydride was removed by adding water to the solution and extracting the product three time with dichloromethane. The combined dichloromethane extracts were washed twice with water and dried over magnesium sulfate. The solution was filtered and solvent removed under reduced pressure. Yield 0.173 g (24%).

Characterizing data for 4: ^{1}H NMR (CD_2Cl_2) δ 8.27 (dd, J = 14.0, 12.7 Hz, 1H), 8.20 (d, J = 12.7 Hz, 1H), 7.61 (d, J = 14.1 Hz, 1H), 7.45 (m, 6H), 7.35 (d, J = 4.1 Hz, 1H), 7.27 (m, 4H), 7.12 (d, J = 15.3 Hz, 1H), 6.96 (d, J = 4.1 Hz, 1H), 6.88 (d, J = 4.1 Hz, 1H), 6.59 (d, J = 15.4 Hz, 1H), 5.96 (d, J = 4.2 Hz, 1H), 3.24 (t, J = 5.6 Hz, 4H), 1.70 (m, 4H), 1.62 (m, 2H). High resolution MS calcd for $C_{26}H_{29}N_3O_2S_3$: 607. 1428. Found: 607.1422.

Reaction procedure for 3,5-bis-(4-hydroxyphenyl)-thiobarbituric acid.

1. 3,5-bis-(4-acetoxyphenyl)-thiourea.

4-aminophenol (100g, 0.916 mol) and thiophosgene (35 ml, 0.458 mol) were added alternately and in portions to 1 L of deionized water while it was being cooled in an ice bath. The reaction vessel was shaken vigorously for several minutes after each addition of reactant. A brown oil formed quickly with evolution of heat. After stirring ~15-20 minutes, solid sodium carbonate (65g, 0.47 mol) was added in small portions with vigorous shaking between additions. Care must be taken during this process since there is significant gas evolution. After most of the sodium carbonate had been added, a white crystalline solid appeared, as well as small amount of dark material. The dark solid slowly disappeared

I-1604-M2

upon further shaking. The viscous slurry was allowed to stand for 4 hours at which time all of the solid had become white. While the reaction vessel was cooled in an ice bath, sodium hydroxide pellets (55g, 1.4 mol) were added in portions to give dissolution of the white solid to a murky purple solution with evolution of heat. When the reaction solution was cool, it was transferred to a 4 L beaker. Acetic anhydride (116 ml, 1.4 mol) was added slowly to the reaction solution while the reaction solution was being stirred vigorously with a thick glass rod. White solid appears immediately when the acetic anhydride comes in contact with the reaction solution. The reaction mixture quickly becomes a viscous slurry. After all traces of the purple solution had disappeared from the mixture, the mixture was suction filtered over paper and allowed to dry.

2. 3,5-bis-(4-hydroxyphenyl)-thiobarbituric acid.

Finely powdered, crude 3,5-bis-(4-acetoxyphenyl)-thiourea (40.9 g, 0.119 mol) and malonic acid (12.3 g, 0.119 mol) were added to a 1L round bottom flask and the flask shaken thoroughly. Acetyl chloride (19 ml, 0.238 mol) was added and again the mixture was shaken and stirred thoroughly. The flask was then connected to an ethanol bubbler and the reaction was heated in a water bath (100°C) for 5.5 hours. Gas was evolved and the dirty gray mixture became a viscous yellow mass. The reaction mixture was allowed to cool and sit overnight. The mixture was partitioned between 30 ml of dichloromethane and saturated sodium bicarbonate solution. The dichloromethane solution was washed with the sodium bicarbonate solution until addition of concentrated hydrochloric acid to small portions of the sodium bicarbonate solution gave no pale yellow solid. The combined aqueous sodium bicarbonate portions were washed once with dichloromethane. The final volume of aqueous sodium bicarbonate solution was 1 liter. To this solution was added sodium hydroxide pellets (23.9 g, 0.597 mol) which dissolved. The solution was allowed to react over night. The next day, dilute hydrochloric acid was added to the pale yellow reaction solution to precipitate a pale yellow solid. The crude product was suction filtered and allowed to dry and used for the synthesis of 6 and 7 without further purification. Yield, 18.5g (47.4%).

I-1604-m3

Reaction procedure for 6.

Crude 3,5-bis-(4-hydroxyphenyl)-thiobarbituric acid (0.500g, 1.52 mmol) 4-Dimethylaminobenzaldehyde (0.227g, 1.52 mmol) were separately dissolved in ~10 ml and ~4 ml of tetrahydrofuran respectively. With rapid stirring, the 4-dimethylaminobenzaldehyde solution was added to the thiobarbituric acid solution to give an immediate red-orange color. After sitting for 10 minutes, a red-orange solid was precipitated, which was filtered over a medium glass frit under positive pressure and then died in air. Yield, 0.500g (71.5%).

Characterizing data for 6: ^{1}H NMR (d_6-DMSO) δ 9.65 (s, 1H), 8.38 (d, J = 9.4 Hz, 2H), 8.24 (s, 1H), 7.03 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 6.77 (overlapping doublets, 6H) 3.12 (s, 6H). Anal Calcd for $C_{25}H_{21}N_3O_4S$: C, 65.35; H, 4.61. Found: C, 65.28; H, 4.64. MS calcd for $C_{25}H_{21}N_3O_4S$: 459.52. Found: 459.

Reaction procedure for 7.

3,5-bis-(4-hydroxyphenyl)-thiobarbituric acid (0.500g, 1.52 mmol) and 4-Dimethylaminocinnimaldehyde (0.267g, 1.52 mmol) were each separately dissolved in ~10 ml tetrahydrofuran. With rapid stirring, the 4-dimethylaminocinnimaldehyde solution was added to the thiobarbituric acid solution to give an immediate purple color. After sitting for ten minutes, a purple solid was precipitated, which was filtered over a medium glass frit under positive pressure and dried in air. Yield, 0.476g (64.4%).

Characterizing data for 7: ^{1}H NMR (d_6-DMSO) δ 8.26 (dd, J = 14.7, 12.5 Hz, 1H), 8.10 (d, J = 12.4 Hz, 1H), 7.77 (d, J = 14.7 Hz, 1H), 7.59 (d, J = 9.1 Hz, 2H), 7.01 (overlapping doublets, 4H), 6.77 (overlapping doublets, 6H), 3.07 (s, 6H). Anal Calcd for $C_{27}H_{23}N_3O_4S$: C, 66.79; H, 4.77. Found: C, 66.70; H, 4.78. MS calcd for $C_{27}H_{23}N_3O_4S$: 485.56. Found: 485.