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Synthesis of Bioactive Heterocycles : One Pot Regioselective Synthesis of Pyrano[3,2-*f*]benzo[*b*]thiophene Derivatives.†

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Abstract: Regioselective synthesis of hitherto unreported pyrano[3,2-*f*]benzo[*b*]thiophene derivatives (**8a-f**) in 90-95 % yields are reported by the application of a less studied rearrangement of 6-(4-aryloxybut-2-ynylthio)[1]benzopyran-2-ones (**5a-f**) *via* oxidation with *m*-chloroperoxybenzoic acid followed by thermal rearrangement and treatment with methanol. Substrates **5a-f** are prepared by the reaction of 6-mercaptocoumarin (unstable) with 1-aryloxy-4-chlorobut-2-ynes (**4**) in refluxing acetone in the presence of anhydrous potassium carbonate and sodium iodide. 6-Mercaptocoumarin (**3**) is in turn prepared by the zinc-acid reduction of the disulfide (**2**) obtained by the reaction of the diazotised 6-aminocoumarin (**1**) with potassium ethylxanthate followed by decomposition. Pyrano[3,2-*f*]-benzo[*b*]thiophene derivatives (**8a-f**) are easily converted to 1-acetylpyrano[3,2-*f*]benzo[*b*]thiophene-7-one (**12**) when refluxed in acetic acid in the presence of catalytic amount of conc. sulfuric acid for 4 h.

Coumarin derivatives are important for their well-known biological activity.[1] There has been a continuous interest in the synthesis[2] of coumarin derivatives. We have earlier reported[3] the synthesis of a number of heterocycles containing the coumarin moiety. In connection with the synthesis of pyrrolocoumarins and pyrroloquinolones we have applied the Amine Oxide Rearrangement[4] for the construction of the pyrrole ring in both the heterocycles coumarin[5] and quinolone.[6] Recently we have reported the synthesis of thieno[3,2-*f*]quinolin-7(6*H*)-one[7] by the application of the less studied sulfoxide rearrangement[8] for the construction of the thiophene ring in the heterocyclic substrate. Herein we report the synthesis of pyrano[3,2-f]benzo[*b*]thiophene (**8**) by rearrangement of an appropriate sulfoxide.

Results and Discussion:

The starting materials for this study *viz.* 6-(4-aryloxybut-2-ynylthio)[1]benzopyran-2-ones (**5a-f**) were prepared starting from 6-aminocoumarin[9] (**1**). Diazotised 6-aminocoumarin was treated with potassium ethylxanthate and the resulting xanthate was hydrolyzed to give the disulfide **2**. 6-Mercaptocoumarin (**3**) (unstable) was generated *in situ* from the disulfide **2**. This reduction was achieved with zinc-dust in acetic acid

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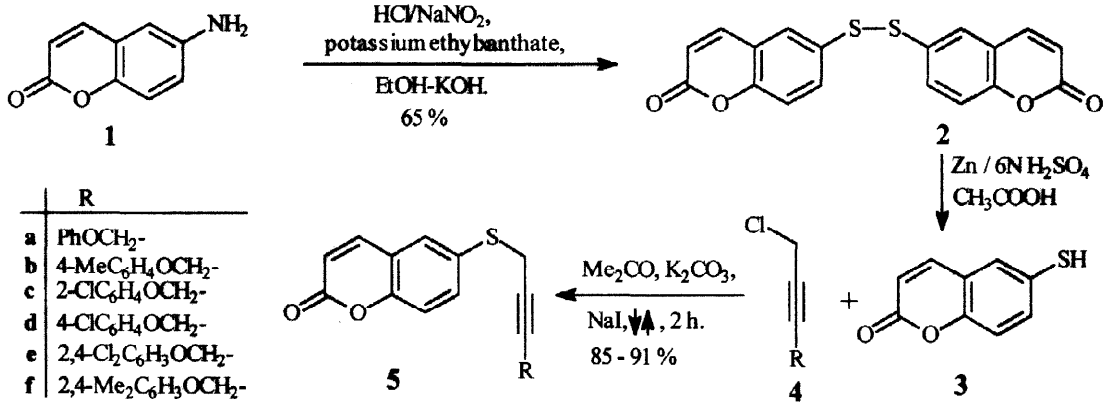
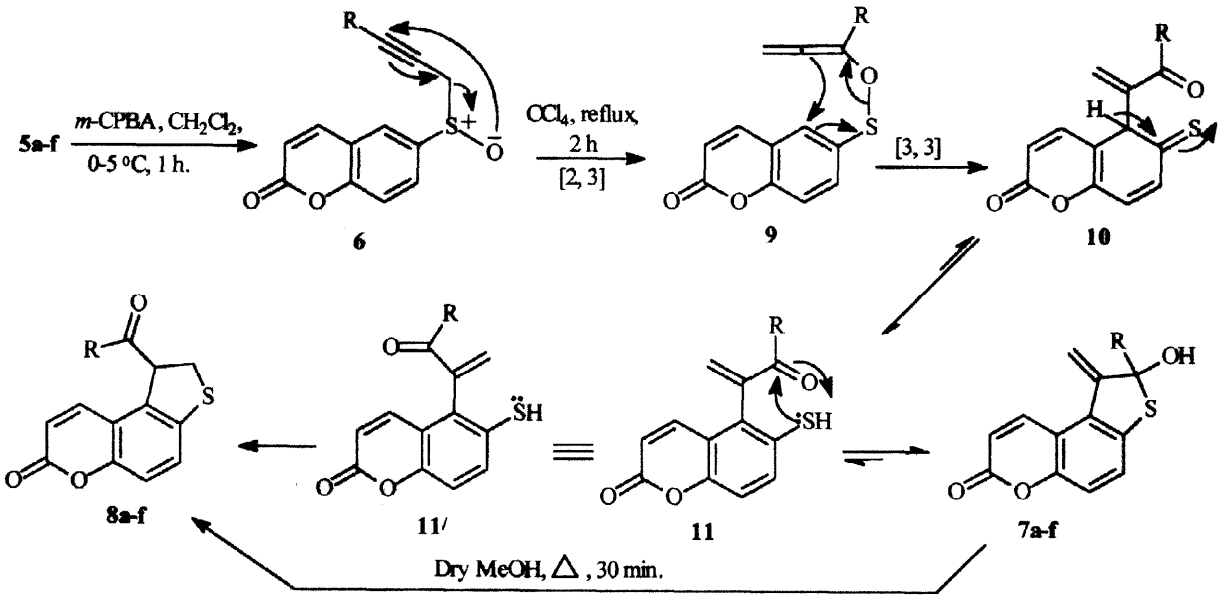
in the presence of 6N sulfuric acid by heating at 80 °C until the solution became clear. This 6-mercapto-coumarin was used without further purification for the synthesis of the substrates **5a-f** in 85-91 % yields by reaction with 1-aryloxy-4-chlorobut-2-ynes (**4**) in refluxing dry acetone in the presence of anhydrous potassium carbonate and sodium iodide (Finkelstein conditions) for 2 h (Scheme 1).



Scheme 1

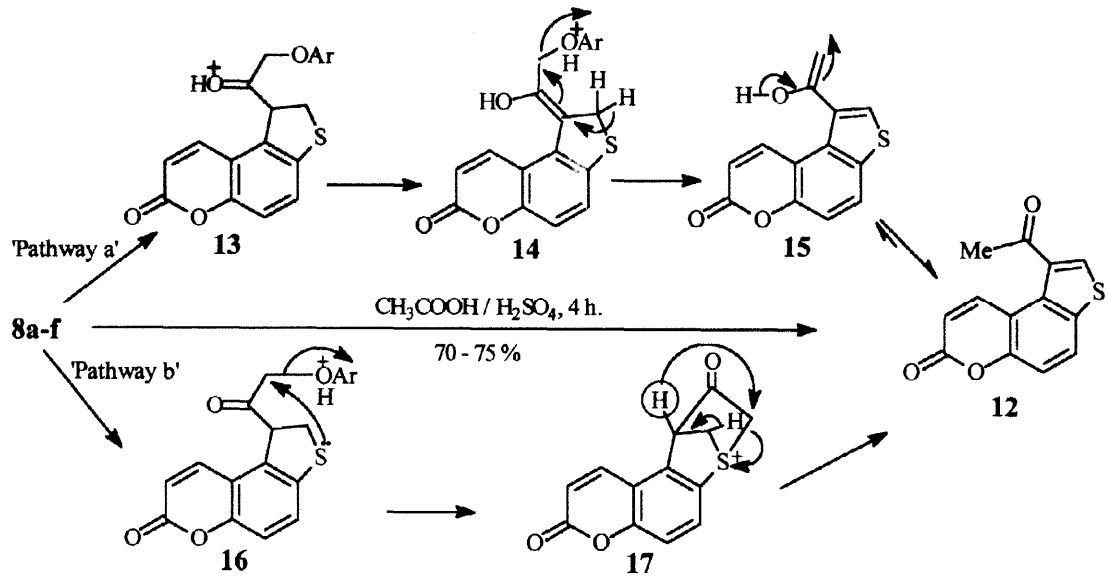
The sulfides **5a-f** were oxidized to the corresponding sulfoxides by slow addition of one equivalent of *m*-chloroperoxybenzoic acid in dichloromethane or carbon tetrachloride solution at 0-5 °C over 1 h (Scheme 2). The thermally labile crude sulfoxide **6a** was refluxed in carbon tetrachloride for 2 h resulting in an inseparable 7:3 mixture of **7a** and **8a**, as judged by IR and ^{1}H-NMR spectroscopy.[10] When this mixture was dissolved in dry methanol component **7a** smoothly converted to **8a** exclusively. The product was characterized from its elemental analysis and spectral data. Encouraged by this result other substrates **6b-f** were also similarly subjected to thermal rearrangement and the resulting mixtures of **7b-f** and **8b-f** were dissolved in methanol by heating to give products **8b-f** in quantitative yields. The selective oxidation of the sulfides **5a-f** to sulfoxides **6a-f** may be conducted in carbon tetrachloride at 0-5 °C. The reaction mixture was then refluxed for 2 h, and carbon tetrachloride was removed. The residual mass was dissolved in dry methanol and heated to give products **8** in 85-90 % overall yield. Thus the whole operation could be conducted in a single pot.

The formation of products **8a-f** from the sulfoxides **6a-f** may be rationalized by the initial [2,3] sigmatropic rearrangement of the sulfoxides to give intermediates **9** followed by a [3,3] sigmatropic rearrangement and enolisation leading to the intermediate **11**, containing an enone moiety favorably juxtaposed to a -SH function for the facile formation of the product monothio-hemiacetal **7** (Scheme 2). The labile monothio-hemiacetals **7** then undergo an internal Michael addition of the thiol on to the enone moiety in **11′** to furnish the pyrano[3,2-*f*]benzo[*b*]thiophene derivatives **8a-f**. The monothio-hemiacetals **7a-f** seem to be very reactive leading to internal Michael addition. In earlier cases,[8] trituration with 20 % potassium hydroxide was necessary to achieve this conversion. In this case simple dissolution of the monothio-hemiacetals in hot methanol is found to be quite satisfactory for this transformation.



Scheme 2

Although we could only get a single product from the sulfoxide rearrangement of each of the substrates studied, and in some cases were able to see from the ^{1}H-NMR spectra that this was the expected angularly fused product. However, in some cases it was quite difficult to ascertain the structure as the aromatic protons were not well separated due to the presence of aryloxy groups in the final product **8**. For this reason we wanted to obtain the final product without an aryloxy group. Therefore, we subjected products **8a-f** to heating in acetic acid in the presence of conc. sulfuric acid for 4 h. Fortunately we were successful in affecting dehydrogenative elimination[11] of phenols from the substrates **8** to give 1-acetylpyrano[3,2-*f*]benzo[*b*]thiophene-7-one (**12**) in 70-75 % yields (Scheme 3). The ^{1}H-NMR of compound **12** showed two well-separated *ortho*-



Scheme 3

coupled aromatic protons at δ 7.45 (d, 1H, J = 9 Hz) and 7.97 (d, 1H, J = 9 Hz) as well as two protons at δ 6.48 (d, 1H, J = 9.5 Hz) and 8.94 (d, 1H, J = 9.5 Hz) due to vinylic protons of the coumarin moiety. The presence of the former two *ortho*-coupled protons conclusively shows this product to be the angularly fused thienocoumarin.

The method is found to be general for the regioselective synthesis of thienocoumarins in excellent yields. This is also an example of the application of a sulfoxide rearrangement in heterocyclic substrates to furnish polyheterocycles. It is reported[12] that other thienocoumarins are known to possess antiinflammatory, antipyretic and antiallergic properties. This is an extremely facile and mild synthesis of thienocoumarin derivatives.

Experimental:

Melting points are uncorrected. IR spectra were run on KBr discs. UV absorption spectra were recorded in absolute EtOH. ^{1}H-NMR spectra were determined for solutions in $CDCl_3$ with TMS as internal standard. Elemental analyses and recording of mass spectra were carried out by RSIC (CDRI) Lucknow. Silica gel (60-120 mesh) was used for chromatographic separation.

The 1-aryloxy-4-chlorobut-2-ynes were prepared according to the published procedure.[4b,8b,13]

Procedure for the Preparation of disulfide 2:

In a beaker (100 ml) equipped with a stirrer and a thermometer, immersed in an ice bath were placed conc. hydrochloric acid (4 ml) and crushed ice (6 g). 6-Aminocoumarin (2 g, 12.5 mmol) was slowly added while stirring. The mixture was cooled to 0 ^{0}C and a cold solution of sodium nitrite (2.5 g) in water (5 ml) was slowly added and the temperature was kept below 4 ^{0}C. In a round bottom flask (250 ml) equipped with magnetic stirrer was placed a solution of potassium ethylxanthate (5 g) in water (10 ml). This mixture was warmed to 40-45 ^{0}C and kept in that range during the slow addition (~2 h) of the cold diazonium solution. This reaction mixture was extracted with chloroform (3 x 50 ml) and the extract was washed with water (3 x 40 ml) and dried (Na_2SO_4). Evaporation of chloroform gave a crude solid. This was dissolved in ethanol (20 ml) and the solution was heated to reflux. Solid potassium hydroxide pellets (1.5 g) were slowly added so as to keep the solution boiling. The reaction mixture was then refluxed for 1 h, cooled and then acidified with 6N sulfuric acid (20 ml). This was extracted with chloroform (3 x 50 ml), washed with water (3 x 30 ml) and dried (Na_2SO_4). Evaporation of chloroform gave a crude solid **2**. This may be used without further purification in the subsequent reaction for the preparation of sulfides. However, an analytical sample was prepared by column chromatographic purification over silica gel. The column was eluted with benzene-ethyl acetate (1:1) to give compound **2**, yield 2.875 g, 65 %; as yellow powder, mp 228 ^{0}C; λ_{max}/nm 245 (log ε 4.19), 276 (log ε 4.09), 330 (log ε 3.56); ν_{max}/cm^{-1} 1710, 1590, 1540, 1460, 1420; δ_H (300 MHz) 6.48 (d, J = 9.5 Hz, 2H), 7.34 (d, J = 9 Hz, 2H), 7.60-7.69 (m, 6H); m/z 354 (M^+), (Found: C, 61.21; H, 3.02. $C_{18}H_{10}O_4S_2$ requires C, 61.02; H, 2.82%).

General Procedure for the Preparation of 6-(4-Aryloxybut-2-ynylthio)[1]benzopyran-2-ones (5a-f):

Zinc dust (1 g) was added to the crude disulfide **2** (0.885 g, 2.5 mmol) in 6N sulfuric acid (20 ml). This was heated on a water bath until the reaction mixture becomes clear. This was extracted with chloroform (3 x 25 ml), washed with water (3 x 20 ml) and dried (Na_2SO_4). Evaporation of solvent gave thiol **3** as a viscous liquid. This was refluxed with the 1-aryloxy-4-chlorobut-2-yne (2.5 mmol) in dry acetone (100 ml) in the presence of anhydrous potassium carbonate (1 g) and a catalytic amount of sodium iodide for 2 h. After cooling the reaction was filtered, solvent was removed from the filtrate. The residual mass was extracted with chloroform (3 x 25 ml). This extract was washed with water (3 x 20 ml) and dried (Na_2SO_4). Evaporation of chloroform gave a crude viscous mass which was purified by column chromatography using benzene-ethyl acetate (3:1) to furnish the sulfides **5a-f.**

6-(4-Phenoxybut-2-ynylthio)[1]benzopyran-2-one (5a), yield 0.725 g, 90 %; Viscous liquid; λ_{max}/nm 223 (log ε 4.26), 266 (log ε 4.16), 323 (log ε 3.58); ν_{max}/cm^{-1} 1710, 1465, 1360, 1230; δ_H (100 MHz) 3.64 (t, J = 1.5 Hz, 2H), 4.66 (t, J = 1.5 Hz, 2H), 6.42 (d, J = 9.5 Hz, 1H), 6.82-7.10 (m, 3H), 7.16-7.40 (m, 3H), 7.44-7.70 (m, 3H); m/z 322 (M^+); (Found: C, 71.09; H, 4.57. $C_{19}H_{14}O_3S$ requires C, 70.81; H, 4.35 %).

6-[4-(4′-Methylphenoxy)but-2-ynylthio][1]benzopyran-2-one (5b), yield 0.730 g, 87 %; as yellowish powder, mp 97 ^{0}C; λ_{max}/nm 224 (log ε 4.47), 267 (log ε 4.29), 330 (log ε 3.62); ν_{max}/cm^{-1} 1715, 1500, 1370, 1225; δ_H (300 MHz) 2.30 (s, 3H), 3.65 (t, J = 1.5 Hz, 2H), 4.65 (t, J = 1.5 Hz, 2H), 6.42 (d, J = 9.5 Hz, 1H), 6.81 (d, J = 9 Hz, 2H), 7.06 (d, J = 9 Hz, 2H), 7.24 (d, J = 9 Hz, 1H), 7.45-7.60 (m, 3H); m/z 336 (M^+); (Found: C, 71.62; H, 4.97. $C_{20}H_{16}O_3S$ requires C, 71.43; H, 4.76 %).

6-[4-(2′-Chlorophenoxy)but-2-ynylthio][1]benzopyran-2-one (5c), yield 0.750 g, 85 %; as white needle, mp 111 ^{0}C; λ_{max}/nm 226 (log ε 4.38), 266 (log ε 4.18), 330 (log ε 3.54); ν_{max}/cm^{-1} 1690, 1565, 1540, 1460, 1355, 1210; δ_H (100 MHz) 3.62 (t, J = 1.5 Hz, 2H), 4.65 (t, J = 1.5 Hz, 2H), 6.43 (d, J = 9.5 Hz, 1H), 6.82 (d, J = 9 Hz, 2H), 7.12-7.32 (m, 3H), 7.48-7.64 (m, 3H); m/z 358, 356 (M^+); (Found: C, 64.21; H, 3.82. $C_{19}H_{13}ClO_3S$ requires C, 64.04; H, 3.65 %).

6-[4-(4′-Chlorophenoxy)but-2-ynylthio][1]benzopyran-2-one (5d), yield 0.780 g, 88 %; as white powder, mp 104 ^{0}C; λ_{max}/nm 224 (log ε 4.44), 267 (log ε 4.36), 323 (log ε 3.72); ν_{max}/cm^{-1} 1715, 1475, 1285, 1220; δ_H (100 MHz) 3.64 (t, J = 1.5 Hz, 2H), 4.74 (t, J = 1.5 Hz, 2H), 6.42 (d, J = 9.5 Hz, 1H), 6.84-7.45 (m, 5H), 7.58-7.71 (m, 3H); m/z 358, 356 (M^+); (Found: C, 63.84; H, 3.45. $C_{19}H_{13}ClO_3S$ requires C, 64.04; H, 3.65 %).

6-[4-(2′,4′-Dichlorophenoxy)but-2-ynylthio][1]benzopyran-2-one (5e), yield 0.885 g, 91 %; as white powder, mp 108 ^{0}C; λ_{max}/nm 228 (log ε 4.12), 266 (log ε 3.95), 323 (log ε 3.33); ν_{max}/cm^{-1} 1720, 1555, 1475, 1370, 1285, 1240; δ_H (100 MHz) 3.62 (t, J = 1.5 Hz, 2H), 4.72 (t, J = 1.5 Hz, 2H), 6.44 (d, J = 9.5 Hz, 1H), 6.85 (d, J = 9 Hz, 1H), 7.03 (d, J = 2.5 Hz, 1H), 7.09-7.40 (m, 2H), 7.46-7.68 (m, 3H); m/z 394, 392, 390 (M^+); (Found: C, 58.63; H, 2.88. $C_{19}H_{12}Cl_2O_3S$ requires C, 58.46; H, 3.08 %).

6-[4-(2′,4′-Dimethylphenoxy)but-2-ynylthio][1]benzopyran-2-one (5f), yield 86 %; Viscous liquid; λ_{max}/nm 235 (log ε 4.44), 274 (log ε 4.26), 317 (log ε 3.84); ν_{max}/cm^{-1} 1720, 1585, 1480, 1375, 1240; δ_H (100 MHz) 2.15 (s, 3H), 2.24 (s, 3H), 3.64 (t, J = 1.5 Hz, 2H), 4.65 (t, J = 1.5 Hz, 2H), 6.48 (d, J = 9.5 Hz, 1H), 6.66-7.01 (m, 2H), 7.12-7.79 (m, 2H), 7.62-7.82 (m, 3H); m/z 350 (M^+); (Found: C, 72.17; H, 4.95. $C_{21}H_{18}O_3S$ requires C, 72.00; H, 5.14 %).

General Procedure for the Pyrano[3,2-*f*]benzo[*b*]thiophene derivatives (8a-f):

m-Chloroperoxybenzoic acid (50 %, 0.345 g, 1 mmol) in dichloromethane (30 ml) was slowly added to a well stirred solution of the disulfide **5a-f** (1 mmol) in dichloromethane (20 ml) at 0-5 ^{0}C over a period of 1 h. The mixture was stirred for half an hour, the solution was washed with 5 % sodium carbonate solution (2 x 20 ml) to remove the organic acid, then water (2 x 20 ml) and dried (Na_2SO_4). The solvent was removed and the residue was refluxed in carbon tetrachloride (20 ml) for 2 h. The reaction mixture was cooled to give a yellow solid. This was found to be a mixture of 7 (~70 %) and 8 (~30 %). Then this solid was dissolved in dry methanol (20 ml) by heating over a period of 30 min. Crystalline solids **8a-f** were obtained in almost quantitative yields when the methanolic solution was cooled.

1,2-Dihydro-1-(phenoxyacetyl)pyrano[3,2-*f*]benzo[*b*]thiophene-7-one (8a), yield 95 %; white crystal, mp 154 ^{0}C; λ_{max}/nm 224 (log ε 4.28), 250 (log ε 4.10), 272 (log ε 4.19); ν_{max}/cm^{-1} 1730, 1700, 1580, 1475, 1425, 1235; δ_H (300 MHz) 3.75 (dd, J = 12, 1.8 Hz, 1H), 4.03 (dd, J = 12, 9 Hz, 1H), 4.74 (d, J = 16.5 Hz, 1H), 4.89 (d, J = 16.5 Hz, 1H), 4.93 (dd, J = 9, 1.8 Hz, 1H), 6.44 (d, J = 9.5 Hz, 1H), 6.91 (d, J = 9 Hz, 2H), 7.06-7.11 (m, 1H), 7.27-7.38 (m, 3H), 7.44 (d, J = 9 Hz, 1H), 7.51 (d, J = 9.5 Hz, 1H); m/z 338 (M^+); (Found: C, 67.56; H, 4.32. $C_{19}H_{14}O_4S$ requires C, 67.45; H, 4.14 %).

1,2-Dihydro-1-(4′-methylphenoxyacetyl)pyrano[3,2-*f*]benzo[*b*]thiophene-7-one (8b), yield 90 %; as white crystal, mp 180 ^{0}C; λ_{max}/nm 223 (log ε 4.32), 252 (log ε 4.27), 266 (log ε 4.31); ν_{max}/cm^{-1} 1735, 1705, 1505, 1440, 1235; δ_H (300 MHz) 2.31 (s, 3H), 3.70 (dd, J = 12, 1.8 Hz, 1H), 3.98 (dd, J = 12, 9 Hz, 1H), 4.68 (d, J = 16.5 Hz, 1H), 4.84 (d, J = 16.5 Hz, 1H), 4.91 (dd, J = 9, 1.8 Hz, 1H), 6.37 (d, J = 9.5 Hz, 1H), 6.73 (d, J = 9 Hz, 2H), 7.10 (d, J = 9 Hz, 2H), 7.21 (d, J = 9 Hz, 1H), 7.36 (d, J = 9 Hz, 1H), 7.42 (d, J = 9.5 Hz, 1H); m/z 352 (M^+); (Found: C, 68.37; H, 4.65. $C_{20}H_{16}O_4S$ requires C, 68.18; H, 4.54 %).

1-(2′-Chlorophenoxyacetyl)-1,2-dihydropyrano[3,2-*f*]benzo[*b*]thiophene-7-one (8c), yield 94 %; as yellow crystal, mp 194 ^{0}C; λ_{max}/nm 225 (log ε 4.36), 274 (log ε 4.10); ν_{max}/cm^{-1} 1735, 1700, 1585, 1480, 1435, 1260, 1240; δ_H (200 MHz) 3.74 (dd, J = 12, 1.8 Hz, 1H), 4.06 (dd, J = 12, 9 Hz, 1H), 4.74 (d, J = 16.5 Hz, 1H), 4.90 (d, J = 16.5 Hz, 1H), 5.06 (dd, J = 9, 1.8 Hz, 1H), 6.41 (d, J = 9.5 Hz, 1H), 6.81 (d, J = 9 Hz, 1H), 6.98-7.06 (m, 1H), 7.20-7.28 (m, 2H), 7.42-7.47 (m, 2H), 7.53 (d, J = 9.5 Hz, 1H); m/z 374, 372 (M^+); (Found: C, 61.12; H, 3.67. $C_{19}H_{13}ClO_4S$ requires C, 61.29; H, 3.49 %).

1-(4′-Chlorophenoxyacetyl)-1,2-dihydropyrano[3,2-*f*]benzo[*b*]thiophene-7-one (8d), yield 90 %; as

white crystal, mp 180 ^{0}C; λ_{max}/nm 225 (log ε 4.15), 275 (log ε 3.98); ν_{max}/cm^{-1} 1720, 1695, 1575, 1460, 1420, 1245; δ_H (300 MHz) 3.73 (dd, J = 12, 1.8 Hz, 1H), 4.03 (dd, J = 12, 9 Hz, 1H), 4.71 (d, J = 16.5 Hz, 1H), 4.85 (d, J = 9, 1.8 Hz, 1H), 4.90 (d, J = 16.5 Hz, 1H), 6.48 (d, J = 9.5 Hz, 1H), 6.82 (d, J = 9 Hz, 2H), 7.30 (d, J = 9 Hz, 3H), 7.45 (d, J = 9 Hz, 1H), 7.58 (d, J = 9.5 Hz, 1H); m/z 374, 372 (M^+); (Found: C, 61.43; H, 3.65. $C_{19}H_{13}ClO_4S$ requires C, 61.29; H, 3.49 %).

1-(2′,4′-Dichlorophenoxyacetyl)-1,2-dihydropyrano[3,2-*f*]benzo[*b*]thiophene-7-one (8e), yield 95 %; as white crystal, mp 204 ^{0}C; λ_{max}/nm 227 (log ε 4.35), 252 (log ε 4.24), 267 (log ε 4.28); ν_{max}/cm^{-1} 1715, 1695, 1575, 1460, 1415, 1240; δ_H (300 MHz) 3.76 (dd, J = 12, 1.8 Hz, 1H), 4.09 (dd, J = 12, 9 Hz, 1H), 4.76 (d, J = 16.5 Hz, 1H), 4.93 (d, J = 16.5 Hz, 1H), 5.03 (dd, J = 9, 1.8 Hz, 1H), 6.48 (d, J = 9.5 Hz, 1H), 6.76 (d, J = 9 Hz, 1H), 7.24 (dd, J = 9, 2.5 Hz, 1H), 7.30 (d, J = 9 Hz, 1H), 7.45 (d, J = 9 Hz, 1H), 7.48 (d, J = 2.5 Hz, 1H), 7.60 (d, J = 9.5 Hz, 1H); m/z 410, 408, 406 (M^+); (Found: C, 56.29; H, 3.15. $C_{19}H_{12}Cl_2O_4S$ requires C, 56.16; H, 2.95 %).

1,2-Dihydro-1-(2′,4′-dimethylphenoxyacetyl)pyrano[3,2-*f*]benzo[*b*]thiophene-7-one (8f), yield 92 %; as white crystal, mp 156 ^{0}C; λ_{max}/nm 224 (log ε 4.45), 252 (log ε 4.22), 273 (log ε 4.32); ν_{max}/cm^{-1} 1735, 1700, 1580, 1480, 1415, 1440, 1215; δ_H (300 MHz) 2.32 (s, 6H), 3.76 (dd, J = 12, 1.8 Hz, 1H), 4.03 (dd, J = 12, 9 Hz, 1H), 4.74 (d, J = 16.5 Hz, 1H), 4.89 (d, J = 16.5 Hz, 1H), 4.92 (dd, J = 9, 1.8 Hz, 1H), 6.43 (d, J = 9.5 Hz, 1H), 6.58 (d, J = 9 Hz, 1H), 6.97 (dd, J = 9, 2.5 Hz, 1H), 7.06 (d, J = 2.5 Hz, 1H), 7.30 (d, J = 9 Hz, 1H), 7.42 (d, J = 9 Hz, 1H), 7.46 (d, J = 9.5 Hz, 1H); m/z 366 (M^+); (Found: C, 68.99; H, 4.78. $C_{21}H_{18}O_4S$ requires C, 68.85; H, 4.92 %).

Conversion of pyrano[3,2-*f*]benzo[*b*]thiophene derivatives (8a-f) to 1-acetylpyrano[3,2-*f*]benzo[*b*]-thiophene-7-one (12):

A solution of the compound **8a-f** (0.5 mmol) in acetic acid (2 ml) and conc. sulfuric acid (1 drop) was refluxed for 4 h. After cooling the reaction mixture was poured into ice-water and extracted with chloroform (3 x 25 ml). The extract was washed with brine (3 x 20 ml) and dried (Na_2SO_4). Evaporation of solvent gave a crude mass which was subjected to column chromatography using benzene-ethyl acetate (3:1) to furnish product **12**.

1-Acetylpyrano[3,2-*f*]benzo[*b*]thiophene-7-one (12), yield 70-75 %; as white powder, mp 206 ^{0}C; λ_{max}/nm 223 (log ε 4.24), 314 (log ε 3.82), 336 (log ε 3.84); ν_{max}/cm^{-1} 1730, 1695, 1475, 1420, 1235; δ_H (300 MHz) 2.78 (s, 3H), 6.48 (d, J = 9.5 Hz, 1H), 7.45 (d, J = 9 Hz, 1H), 7.97 (d, J = 9 Hz, 1H), 8.44 (s, 1H), 8.94 (d, J = 9.5 Hz, 1H); m/z 244 (M^+); (Found: C, 63.81; H, 3.37. $C_{13}H_8O_3S$ requires C, 63.93; H, 3.28 %).

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References and Notes:

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10. Compounds **7a-f** were not obtained in the pure form. However, their presence was indicated in the mixture with **8a-f** from IR and ^{1}H-NMR spectra of the mixtures. The IR absorption band at 3400 cm^{-1} indicated the presence of -OH function. The ^{1}H-NMR of the mixture showed signals for **7a** at δ 3.64 (br.s, 1H, D_2O exchangeable), 4.22 (d, J = 10 Hz, 1H) and 4.34 (d, J = 10 Hz, 1H) due to diastereotopic protons of methylene adjacent to chiral centre, 5.86 (s, 1H) and 5.97 (s, 1H) due to protons of exomethylene. Similar ^{1}H-NMR signals were also observed for other compounds **7b-f** in the mixtures. As compounds **7a-f** have not been fully characterized the structure **7a-f** are tentative.
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