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Reaction of β-Ethylsulfanylpropionyl Tetrafluoroborate with Halogen-containing Aromatic and Heteroaromatic Compounds

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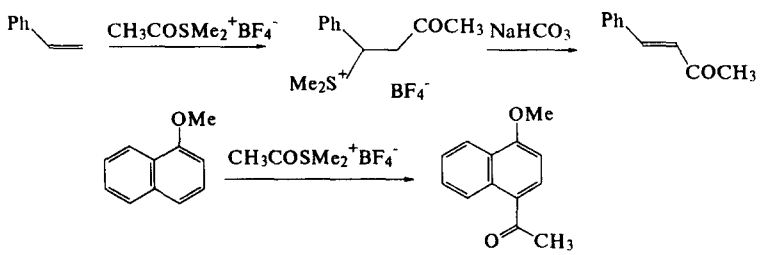
Abstract: Acylation of halogen-containing electron-rich aromatic and heteroaromatic compounds with β-ethylsulfanylpropionyl tetrafluoroborate leads to the formation of 6-membered sulfonium salts fused with aromatic or heteroaromatic rings. Base induced cleavage of sulfonium salts gave ethylsulfanyl substituted aryl vinyl ketones. Cyclic sulfonium salts can also be converted into corresponding thiopyran-4-ones by treatment with thiourea in MeOH. © 1998 Elsevier Science Ltd. All rights reserved.

Modification of active electrophilic reagents by complexation with different nucleophiles is a convenient way to new reagents, which in most cases act more selectively and more mildly. [1]

Acyldimethylsulfonium salts, obtained by treatment the corresponding acyl tetrafluoroborates with methyl sulfide, are known to react with different unsaturated hydrocarbons, aromatic and heteroaromatic compounds (Scheme 1). The high yields and low amount of side products and polymers make acylsulfonium salts useful reagents in organic synthesis.[2,3] Also, it was reported, that the complex of trifluoroacetic anhydride with boron trifluoride and methyl sulfide, having the structure of an acyldimethylsulfonium salt, is a useful reagent for trifluoroacylation of various unsaturated hydrocarbons and aromatic compounds.[3,4]



Scheme 1

In the preceding papers, we have proposed an intramolecular modification of acylsulfonium salts - β-ethylsulfanylpropionyl tetrafluoroborate **1**. Obtained as shown on Scheme 2, **1** is quite stable at the temperature below -30°C, and reacts with different unsaturated hydrocarbons. Reaction of **1** with

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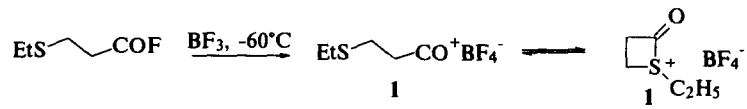
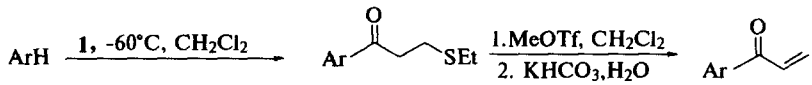
alkenes and acetylenes proceeds as conjugate addition of acyl moiety and sulfide to a double or triple C-C bond which results in formation of the corresponding six-membered sulfonium salts.[5]



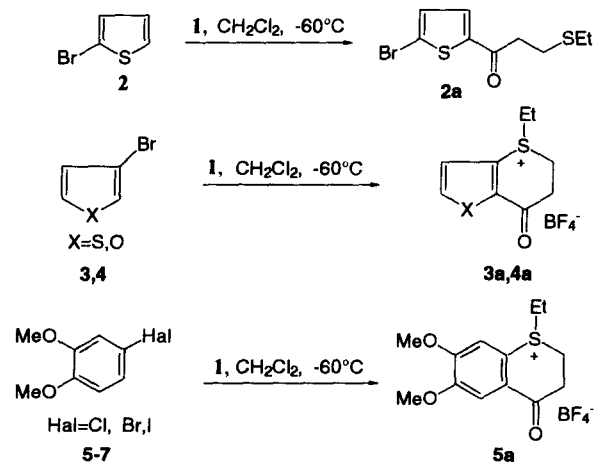
Scheme 2

Recently, we have investigated the acylation of various aromatics with the complex of β-ethylsulfanylpropionyl fluoride/boron trifluoride. This reaction leads to formation of 3-(ethylsulfanyl)-1-(aryl)-1-propanones in good yields. The latter can easily be converted to aryl vinyl ketones in excellent yields (Scheme 3).



Scheme 3

Now we report unusual behaviour of some halogen-containing aromatic compounds in the reaction with **1**. The reaction of 2-bromothiophene **2** with **1** leads to 1-(5-bromo-2-thienyl)-3-(ethylsulfanyl)-1-propanone **2a**, but in the case of 3-bromothiophene **3** the corresponding 6-membered sulfonium salt **3a** was formed instead of 1-(3-bromothienyl)-3-ethylsulfanylpropan-1-one (Scheme 4).



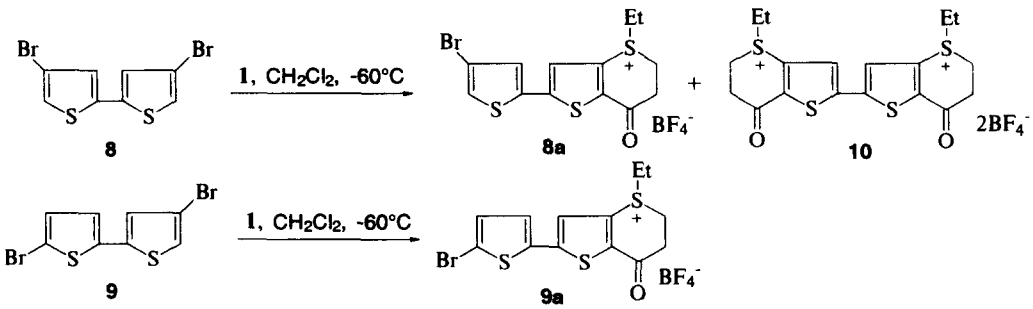
Scheme 4

It was found that reactions of **1** with some other halogen-containing aromatic compounds, *e.g.* 3-bromofurane **4**, 1,2-dimethoxy-4-halobenzenes **5-7**, proceed analogously to give the products of substitution of halogen atom with sulfide **4a**, **5a**. However, our attempt to perform the acylation of 3-bromoanisole with **1** was unsuccessful because of its low reactivity.

We suppose that the reaction proceeds stepwise. The first step is electrophilic acylation of aromatic ring, the next step is nucleophilic substitution of halogen atom by sulfide moiety to form a 6-membered sulfonium salt ring junction. The second step can be achieved only if the carbonyl group enters ortho to

halogen. In the cases of reactions of **1** with 2-bromothiophene **2** and bromoferrocene no products of intra- or intermolecular formation of sulfonium salts were detected.

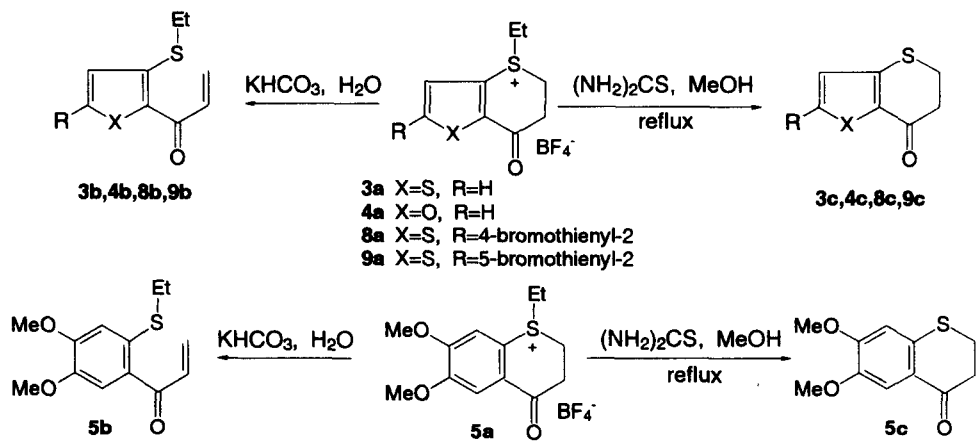
Also we have studied the reactions of **1** with dibromo-substituted bithiophenes **8** and **9** (Scheme 5). In the case of bithiophene **8** the product of diacylation **10** was expected. With a molar ratio of **1** and **8** 2:1 the mixture of products of mono- and diacylation **8a** and **10** (3:1) was obtained. Increasing the molar ratio of starting **1** and **8** to 4:1 did not affect the ratio of products. Washing of the mixture of sulfonium salts **8a** and **10** with cold methanol permits isolation of **8a** in pure form.



Scheme 5

To study the influence of the halogen nature on the reaction we have carried out the reactions of **1** with 4-iodo, 4-bromo and 4-chloro-1,2-dimethoxybenzenes **5-7**. Yields of sulfonium salt **5a** were found to decrease in the order I, Br, Cl.

We have also studied some reactions of cyclic sulfonium salts **3a-5a,8a,9a**. Base promoted cleavage of sulfonium salts (aqueous solution of $KHCO_3$) leads to formation of the corresponding ethylsulfanylaryl vinyl ketones **3b-5b,8b,9b** in quantitative yield. Reflux of sulfonium salts with thiourea in MeOH affords the corresponding thiopyran-4-ones **3c-5c,8c,9c** in good yields (Scheme 6). We believe that these products are formed by nucleophilic substitution at the ethyl group of the sulfonium moiety.



Scheme 6

In summary, reactions of β-ethylsulfanylpropionyl tetrafluoroborate **1** with halogen-containing aromatic and heteroaromatic compounds give rise to cyclic sulfonium salts **3a-5a,8a,9a**, which can be converted to ethylsulfanylaryl vinyl ketones **3b-5b,8b,9b** or thiopyran-4-ones **3c-5c,8c,9c**.

Experimental section

Melting points were determined in sealed capillaries and are uncorrected. NMR spectra were recorded on Varian VXR-400 and Bruker AM 400C spectrometers in CD_3CN, $CDCl_3$ or $CDCl_3/CF_3COOH$ 4/1 with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer. Column chromatography was performed on silica gel (63-200 mesh, Merck). All solvents used were dried and distilled according to the standard procedures. β-Ethylsulfanylpropionyl fluoride was prepared according to the literature procedure[4] from 3-mercaptopropionic acid (Merck). Compounds **8** and **9** were synthesized from 5,5'-dibromo-2,2'-bithiophene[6] using the literature procedures[7].

General procedure for sulfonium salts

A well-stirred solution of β-ethylsulfanylpropionyl fluoride (0.02 mol) in dichloromethane (40 mL) was saturated by gaseous BF_3 at -60°C. A solution of corresponding aromatic compound (0.02 mol) in dichloromethane (10 mL) was added dropwise. After stirring for 15 min at -40°C the temperature was allowed to rise to 0 °C and the mixture was stirred for two hours at this temperature. The reaction mixture was poured into dry ether (80 mL). The precipitated sulfonium salt was collected by vacuum filtration, washed with dry ether (20 mL), cold methanol (10 mL), dry ether (30 mL) and dried *in vacuo*.

4-Ethyl-7-oxo-6,7-dihydro-5*H*-thieno[3,2-*b*]thiopyran-4-ium-tetrafluoroborate (3a), yield 33%. mp 123-125 °C(dec.). IR (Nujol) (ν,cm^{-1}): 1680 (CO). ^{1}H NMR (400MHz, CD_3CN, δ ppm): 8.20 (d, 1H, ^{3}J=5.2 Hz, H-5 thiophene), 7.61 (d, 1H, ^{3}J=5.2 Hz, H-4 thiophene), 4.19 (ddd, 1H, ^{3}J=4.2 Hz, ^{3}J=11.1 Hz, ^{2}J=14.6 Hz, S*CH*$_2$CH$_2$), 4.01 (ddd, 1H, ^{3}J=^{3}J=4.8 Hz, ^{2}J=14.6 Hz, S*CH*$_2$CH$_2$), 3.76-3.61 (m, 2H, S*CH*$_2$CH$_3$), 3.08 (ddd, 1H, ^{3}J=4.2 Hz, ^{3}J=11.1 Hz, ^{2}J=18.4 Hz, SCH$_2$*CH*$_2$), 3.12 (ddd, 1H, ^{3}J=^{3}J=4.8 Hz, ^{2}J=18.4 Hz, SCH$_2$*CH*$_2$), 1.44 (t, 3H, ^{3}J=7.2 Hz, CH_3). ^{13}C NMR (100MHz, CD_3CN, δ ppm): 185.36 (C=O), 142.91, 138.16, 130.46, 124.67 (4C aromatic), 39.87, 35.93, 32.12 (3 CH_2), 9.71 (CH_3). Elemental analysis(%): found: C, 37.62; H, 3.74; Calc. for $C_9H_{11}BF_4OS_2$: C, 37.78; H, 3.88.

4-Ethyl-7-oxo-6,7-dihydro-5*H*-thiopyrano[3,2-*b*]furan-4-ium-tetrafluoroborate (4a), yield 19%. mp 105-107 °C (dec.). IR (Nujol) (ν,cm^{-1}): 1700 (CO). ^{1}H NMR (400MHz, CD_3CN, δ ppm): 7.85 (d, 1H, ^{3}J=2.0 Hz, H-5 furane), 6.91 (d, 1H, ^{3}J=2.0 Hz, H-4 furane), 3.99 (ddd, 1H, ^{3}J=4.0 Hz, ^{3}J=10.8 Hz, ^{2}J=14.4 Hz, S*CH*$_2$CH$_2$), 3.76 (ddd, 1H, ^{3}J=4.2 Hz, ^{3}J=5.8 Hz, ^{2}J=14.4 Hz, S*CH*$_2$CH$_2$), 3.58-3.42 (m, 2H, S*CH*$_2$CH$_3$), 3.12 (ddd, 1H, ^{3}J=4.2 Hz, ^{3}J=10.8 Hz, ^{2}J=18.4 Hz, SCH$_2$*CH*$_2$), 2.92 (ddd, 1H, ^{3}J=4.0 Hz, ^{3}J=5.8 Hz, ^{2}J=18.4 Hz, SCH$_2$*CH*$_2$), 1.27 (t, 3H, ^{3}J=7.2 Hz, CH_3). ^{13}C NMR (100MHz, CD_3CN,

δ ppm): 180.41 (C=O), 150.49, 149.26, 117.52, 113.45 (4 C aromatic), 39.74, 36.70, 33.70 (3 CH_2), 9.63 (CH_3). Elemental analysis(%): found: C, 39.82; H, 4.24; Calc. for $C_9H_{11}BF_4O_2S$: C, 40.03; H, 4.11.

1-Ethyl-6,7-dimethoxy-4-oxo-3,4-dihydro-2*H*-thiochromenium-tetrafluoroborate (5a), from 4-chloro-1,2-dimethoxybenzene yield 12%; from 4-bromo-1,2-dimethoxybenzene yield 38%; from 4-iodo-1,2-dimethoxybenzene yield 45%. mp >230 °C (dec.). IR (Nujol) (ν,cm^{-1}): 1700 (CO). ^1H NMR (400MHz, CD_3CN, δ ppm): 7.75 (s, 1H, H-5), 7.34 (s, 1H, H-8), 4.16-4.12 (m, 1H, S$CH_2$$CH_2$), 3.98 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 3.92-3.85 (m, 1H, S$CH_2$$CH_2$), 3.63 (q, 2H, ^3J=7.2 Hz, S$CH_2$$CH_3$), 3.32-3.23 (m, 1H, SCH_2CH_2), 3.11-3.06 (m, 1H, SCH_2CH_2), 1.45 (t, 3H, ^3J=7.2 Hz, CH_3). ^{13}C NMR (100MHz, CD_3CN, δ ppm): 187.6 (C=O), 154.1, 153.4, 126.4, 115.7 (4 C, q), 113.8, 111.5 (2CH), 56.8, 56.1 (2 OCH_3), 38.5, 32.5, 29.7 (3 CH_2), 8.8 (CH_3). Elemental analysis(%): found: C, 46.16; H, 5.06; Calc. for $C_{13}H_{17}BF_4O_3S$: C, 45.91; H, 5.04.

2-(4-Bromo-2-thienyl)-4-ethyl-7-oxo-6,7-dihydro-5*H*-thieno[3,2-*b*]thiopyran-4-ium-tetrafluoroborate (8a), yield 52%. mp 203-209 °C (dec.). IR (Nujol) (ν,cm^{-1}): 1670 (CO). ^1H NMR (400MHz, $CDCl_3/CF_3COOH$ 4/1, δ ppm): 7.71 (br.s, 1H, H-3 thiophene), 7.49 (br.s, 2H, H-5 thiophene and H-3 thienothiopyranium), 4.42-4.34 (m, 1H, S$CH_2$$CH_2$), 4.28-4.22 (m, 1H, S$CH_2$$CH_2$), 3.89 (q, 2H, ^3J=7.4 Hz, S$CH_2$$CH_3$), 3.64-3.55 (m, 1H, SCH_2CH_2), 3.51-3.46 (m, 1H, SCH_2CH_2), 1.68 (t, 3H, ^3J=7.4 Hz, CH_3). ^{13}C NMR (100MHz, $CDCl_3/CF_3COOH$ 4/1, δ ppm): 187.16 (C=O), 151.46, 137.84, 134.22 (3 C, q), 131.64, 127.80 (2 CH), 126.24 (C, q), 124.88 (CH), 112.97 (C, q), 40.29, 35.70, 31.19 (3 CH_2), 9.05 (CH_3). Elemental analysis(%): found: C, 34.47; H, 2.72; Calc. for $C_{13}H_{12}BBrF_4OS_3$: C, 34.92; H, 2.71.

***bis*-(4-Ethyl-7-oxo-6,7-dihydro-5*H*-thieno[3,2-*b*]thiopyran-4-ium-2-yl)-ditetrafluoroborate (10),** The ^1H NMR spectrum was obtained by subtraction the spectrum of pure **8a** from the spectrum of the mixture of **8a** and **10**. ^1H NMR (400MHz, $CDCl_3/CF_3COOH$ 4/1, δ ppm): 7.72 (br.s, 2H, H-3 thiophene), 4.42-4.22 (m, 4H, S$CH_2$$CH_2$), 3.75 (q, 4H, ^3J=7.4 Hz, S$CH_2$$CH_3$), 3.64-3.46 (m, 4H, SCH_2CH_2), 1.40 (t, 6H, ^3J=7.4 Hz, CH_3).

2-(5-Bromo-2-thienyl)-4-ethyl-7-oxo-6,7-dihydro-5*H*-thieno[3,2-*b*]thiopyran-4-ium-tetrafluoroborate (9a), yield 41%. mp 192-198 °C (dec.). IR (Nujol) (ν,cm^{-1}): 1670 (CO). ^1H NMR (400MHz, $CDCl_3/CF_3COOH$ 4/1, δ ppm): 7.60 (br.s, 1H, H-3 thienothiopyranium), 7.35 (br.s, 1H, H-3` thiophene), 7.12 (br.s, 1H, H-4` thiophene), 4.45-4.30 (m, 1H, S$CH_2$$CH_2$), 4.25-4.12 (m, 1H, S$CH_2$$CH_2$), 3.95-3.75 (m, 2H, S$CH_2$$CH_3$), 3.70-3.15 (m, 2H, SCH_2CH_2), 1.71 (t, 3H, ^3J=7.4 Hz, CH_3). ^{13}C NMR (100MHz, $CDCl_3/CF_3COOH$ 4/1, δ ppm): 187.04 (C=O), 151.86, 137.05, 134.59 (3C, q), 132.64, 129.70 (2 CH), 126.22 (C, q), 124.32 (CH), 119.19 (C, q), 40.40, 36.71, 31.15 (3 CH_2), 9.06 (CH_3). Elemental analysis(%): found: C, 34.45; H, 2.75; Calc. for $C_{13}H_{12}BBrF_4OS_3$: C, 34.92; H, 2.71.

General procedure for 1-(aryl)-2-propen-1-ones

To a suspension of sulfonium salt in ether an excess of aqueous $KHCO_3$ was added and the reaction mixture was stirred for two hours. The organic layer was separated, the aqueous layer was extracted twice with ether. The combined organic phases were dried (Na_2SO_4), filtered and concentrated at reduced pressure. The crude product was purified by flash chromatography with ethyl acetate/hexane (9/1).

1-[3-(Ethylsulfanyl)-2-thienyl]-2-propen-1-one (3b), yield 83%. mp 67-69 °C. IR (Nujol) (ν,cm^{-1}): 1600, 1640 (C=C, CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.53 (d, 1H, ^{3}J=5.2 Hz, H-5 thiophene), 7.02 (d, 1H, ^{3}J=5.2 Hz, H-4 thiophene), 6.95 (dd, 1H, ^{3}J=16.8 Hz, ^{3}J=10.4 Hz, CH=), 6.43 (dd, 1H, ^{3}J=16.8 Hz, ^{2}J=1.6 Hz, CH_2=), 5.76 (dd, 1H, ^{3}J=10.4 Hz, ^{2}J=1.6 Hz, CH_2=), 2.98 (q, 2H, ^{3}J=7.2 Hz, CH_2), 1.34 (t, 3H, ^{3}J=7.2 Hz, CH_3). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 181.29 (C=O), 146.04 (C, q), 133.09, 131.04 (2CH), 130.68 (C, q), 128.75 (=CH_2), 126.60 (CH), 27.05 (CH_2), 13.68 (CH_3). Elemental analysis(%): found: C, 54.49; H, 4.82; Calc. for $C_9H_{10}OS_2$: C, 54.51; H, 5.08.

1-[3-(Ethylsulfanyl)-2-furyl]-2-propen-1-one (4b), yield 95%; pale yellow oil. IR (Neat) (ν,cm^{-1}): 1600, 1650 (C=C, CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.55 (d, 1H, ^{3}J=1.9 Hz, H-5 furane), 7.15 (dd, 1H, ^{3}J=17.2 Hz, ^{3}J=10.4 Hz, CH=), 6.58 (d, 1H, ^{3}J=1.9 Hz, H-4 furane), 6.51 (dd, 1H, ^{3}J=17.2 Hz, ^{2}J=1.9 Hz, CH_2=), 5.81 (dd, 1H, ^{3}J=10.4 Hz, ^{2}J=1.9 Hz, CH_2=), 2.95 (q, 2H, ^{3}J=7.4 Hz, CH_2), 1.38 (t, 3H, ^{3}J=7.4 Hz, CH_3). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 177.44 (C=O), 146.22 (C, q), 145.61 (CH), 133.81 (C, q), 130.94 (CH), 128.22 (CH_2), 111.18 (CH), 26.12 (CH_2), 13.80 (CH_3). Elemental analysis(%): found: C, 58.95; H, 5.64; Calc. for $C_9H_{10}O_2S$: C, 59.32; H, 5.53.

1-[2-(Ethylsulfanyl)-4,5-dimethoxyphenyl]-2-propen-1-one (5b), yield 88%; colorless oil. IR (Neat) (ν,cm^{-1}): 1610, 1650 (C=C, CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.05 (s, 1H, H-3 aromatic), 6.92 (dd, 1H, ^{3}J=17.2 Hz, ^{3}J=10.4 Hz, CH=), 6.86 (s, 1H, H-6 aromatic), 6.18 (dd, 1H, ^{3}J=17.2 Hz, ^{2}J=1.5 Hz, CH_2=), 5.81 (dd, 1H, ^{3}J=10.4 Hz, ^{2}J=1.5 Hz, CH_2=), 3.86 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 2.80 (q, 2H, ^{3}J=7.4 Hz, CH_2), 1.20 (t, 3H, ^{3}J=7.4 Hz, CH_3). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 191.9 (C=O), 151.0, 146.4, 134.9, 131.1, 130.4, 128.8, 112.3, 112.0 (6 C aromatic, CH=CH_2), 56.0, 55.6 (2 OCH_3), 28.3 (CH_2), 13.3 (CH_3). Elemental analysis(%): found: C, 61.91; H, 6.37; Calc. for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39.

1-[5-(4`-Bromo-2`-thienyl)-3-(ethylsulfanyl)-2-thienyl]-2-propen-1-one (8b), yield 86%. mp 92-95 °C. IR (Nujol) (ν,cm^{-1}): 1610, 1650 (C=C, CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.22 (d, 1H, ^{4}J=1.4 Hz, H-5` thiophene), 7.20 (d, 1H, $^4$J=1.4 Hz, H-3` thiophene), 7.01 (s, 1H, H-4 thiophene), 6.94 (dd, 1H, ^{3}J=16.6 Hz, ^{3}J=10.2 Hz, CH=), 6.49 (dd, 1H, ^{3}J=16.6 Hz, ^{2}J=1.7 Hz, CH_2=), 5.81 (dd, 1H, ^{3}J=10.2 Hz, ^{2}J=1.7 Hz, CH_2=), 3.05 (q, 2H, ^{3}J=7.4 Hz), 1.41 (t, 3H, ^{3}J=7.4 Hz). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 176.31 (C=O), 146.98, 141.02, 136.66, 132.93, 129.11, 127.97, 123.60,

123.07, 110.95 (C, q), 27.39 (CH_2), 13.67 (CH_3). Elemental analysis(%): found: C, 43.55; H, 2.98; Calc. for $C_{13}H_{11}BrOS_3$: C, 43.46; H, 3.09.

1-[5-(5`-Bromo-2`-thienyl)-3-(ethylsulfanyl)-2-thienyl]-2-propen-1-one (9b), yield 95%. mp 66-68 °C. IR (Nujol) (ν,cm^{-1}): 1640 (C=C and CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.12 (d, 1H, ^3J=3.8 Hz, H-3` thiophene), 7.08 (d, 1H, $^3J$=3.8 Hz, H-4` thiophene), 7.07 (s, 1H, H-4 thiophene), 7.01 (dd, 1H, ^3J=16.6 Hz, ^3J=10.2 Hz, CH=), 6.49 (dd, 1H, ^3J=16.6 Hz, ^2J=1.7 Hz, CH_2=), 5.81 (dd, 1H, ^3J=10.2 Hz, ^2J=1.7 Hz, CH_2=), 3.05 (q, 2H, ^3J=7.4 Hz, CH_2), 1.41 (t, 3H, ^3J=7.4 Hz, CH_3). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 176.31 (C=O), 146.98, 141.02, 136.66, 132.93, 129.11, 127.97, 123.60, 123.07, 110.95 (C, q), 27.39 (CH_2), 13.67 (CH_3). Elemental analysis(%): found: C, 43.30; H, 2.79; Calc. for $C_{13}H_{11}BrOS_3$: C, 43.46; H, 3.09.

General procedure for thiopyranes

To a solution of sulfonium salt (0.003 mol) in methanol (15 mL) thiourea (2.3 g, 0.03 mol) and $HClO_4$ (1 mL of 70% aqueous solution) were added. After 48 hours of reflux the reaction mixture was poured into 100 mL of water and extracted with CH_2Cl_2 (4X10 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated at reduced pressure. The crude product was purified by column chromatography with ethyl acetate/hexane (9/1).

5,6-Dihydro-7*H*-thieno[3,2-*b*]thiopyran-7-one (3c), yield 89%; pale yellow oil. IR (Neat) (ν,cm^{-1}): 1640 (CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.62 (d, 1H, ^3J=5.2 Hz, H-5 thiophene), 6.93 (d, 1H, ^3J=5.2 Hz, H-4 thiophene), 3.31-3.28 (m, 2H, SCH_2CH_2), 2.87-2.83 (m, 2H, SCH_2CH_2). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 187.99 (C=O), 145.35, 134.39, 131.44, 127.14 (4C aromatic), 38.34, 28.56 ($2CH_2$). Elemental analysis(%): found: C, 49.22; H, 3.61; Calc. for $C_7H_6OS_2$: C, 49.39; H, 3.55.

5,6-Dihydro-7*H*-thiopyrano[3,2-*b*]furan-7-one (4c), yield 42%; mp 100-103 °C (dec.). IR (Nujol) (ν,cm^{-1}): 1640 (CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.64 (d, 1H, ^3J=2.0 Hz, H-5 furane), 6.53 (d, 1H, ^3J=2.0 Hz, H-4 furane), 3.36-3.32 (m, 2H, SCH_2CH_2), 2.92-2.89 (m, 2H, SCH_2CH_2). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 181.77 (C=O), 147.66, 144.33, 136.14, 111.09 (4C aromatic), 38.80, 28.96 ($2CH_2$). Elemental analysis(%): found: C, 54.69; H, 3.95; Calc. for $C_7H_6O_2S$: C, 54.53; H, 3.92.

6,7-Dimethoxy-2,3-dihydro-4*H*-thiochromen-4-one (5c), yield 67%; colorless oil. IR (Neat) (ν,cm^{-1}): 1670 (CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.59 (s, 1H, H-5), 6.68 (s, 1H, H-8), 3.91 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.24-3.20 (m, 2H, SCH_2CH_2), 2.93-2.90 (m, 2H, SCH_2CH_2). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 192.79 (C=O), 153.50, 147.10, 135.97, 124.08 (4 C, q), 110.37, 108.89 (2CH), 56.12, 55.96 (2 OCH_3), 39.08, 27.14 (2 CH_2). Elemental analysis(%): found: C, 34.45; H, 2.75; Calc. for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39.

2-(4-Bromo-2-thienyl)-5,6-dihydro-7*H*-thieno[3,2-*b*]thiopyran-7-one (8c), yield 48%. mp 71-74 °C. IR (Nujol) (ν,cm^{-1}): 1660 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.26 (d, 1H, ^{4}J=1.4 Hz, H-5 thiophene), 7.23 (d, 1H, ^{4}J=1.4 Hz, H-4 thiophene), 7.02 (s, 1H, H-3 thienothiopyran), 3.38-3.35 (m, 2H, SCH_2CH_2), 2.92-2.89 (m, 2H, SCH_2CH_2). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 187.51 (C=O), 146.30, 144.17, 136.69, 130.17 (4C, q), 128.36, 123.99, 123.34 (3CH), 111.02 (C, q), 38.21, 28.59 ($2CH_2$). Elemental analysis(%): found: C, 39.41; H, 2.33; Calc. for $C_{11}H_7BrOS_3$: C, 39.88; H, 2.13.

2-(5-Bromo-2-thienyl)-5,6-dihydro-7*H*-thieno[3,2-*b*]thiopyran-7-one (9c), yield 70%. mp 60-62 °C. IR (Nujol) (ν,cm^{-1}): 1660 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.26 (d, 1H, ^{3}J=1.4 Hz, H-3 thiophene), 7.23 (d, 1H, ^{3}J=1.4 Hz, H-4 thiophene), 7.02 (s, 1H, H-3 thienothiopyran), 3.38-3.35 (m, 2H, SCH_2CH_2), 2.92-2.89 (m, 2H, SCH_2CH_2). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 187.51 (C=O), 146.30, 144.17, 136.69, 130.17 (4C, q), 128.36, 123.99, 123.34 (3CH), 111.02 (C, q), 38.21, 28.59 ($2CH_2$). Elemental analysis(%): found: C, 39.54; H, 2.17; Calc. for $C_{11}H_7BrOS_3$: C, 39.88; H, 2.13.

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