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ORIGINAL PAPER

Thiophenium-ylides: Synthesis and reactivity

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Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

The reaction of propanedioic acid, 2-diazo-1,3-bis(1,1-dimethylethyl) ester (di-*tert*-butyl diazomalonate) with a series of cyclopenta[*b*]thiophenes in the presence of catalytic rhodium acetate was studied. The resulting S—C ylides underwent a rearrangement to form a heterocycle with different topology; thialene, in very low yields. Experimental and spectral data for all compounds are provided.

Keywords: cyclopenta[*b*]thiophene, thiophenium-ylide, rhodium catalysis, thialene

Introduction

Chemistry of sulfur is a specific branch of organic chemistry, where thiopyran derivatives represent an important sub-class of compounds extensively exploited by nature and mankind. Different types of thiopyran compounds have been synthesized in the past years. In contrast, a limited number of examples of a particular type of thiopyrans/thiopyranium derivatives, those incorporated in pseudoazulenes, were reported. Thialene (cyclopenta[*b*]thiopyran) (Mayer et al., 1961; Mayer & Franke, 1965; Klein & Horák, 1986), an intensively blue–violet heteroarene, although it is isoelectronic with extensively used benzo[*b*]thiophene (benzothiophene) congeners, represents rather an underappreciated structural motive. Pseudoazulenes (Klein & Horák, 1986), iso-π-electronic heteroanalogues of bicyclo[5.3.0]decapentaene (azulene) exhibiting unique spectroscopic properties, have not yet been thoroughly investigated. Due to their low stability but obvious heteroaromaticity (Elguero et al., 1978), they were formerly called "uncommon" arenes. A simple drawing of their resonance structures explains this phenomenon (Mayer et al., 1961) (Fig. 1).

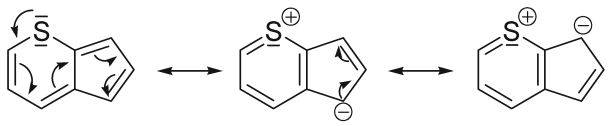

Fig. 1. Canonical structures of thialene.

Recently, the structure and reactivity of thiophenium- and selenophenium-ylides were investigated with the goal to prepare new fused thialene derivatives employing an uncommon thiophene to thiopyran ring expansion (Machara et al., 2004, 2009) in the crucial step (Fig. 2).

This transformation, related to the Stevens rearrangement, has been already investigated and mechanistic aspects were rationalized in a series of papers (Bowles et al., 1985, 1988a, 1988b; Smith, 1990; MacKenzie & Thomson, 1982). In the continuation of our effort, a preliminary study associated with cyclopentathiophenium-ylides and their thermally induced rearrangement evaluation was done in order to find an alternative synthetic way providing the parent thialene derivatives (Fig. 3).

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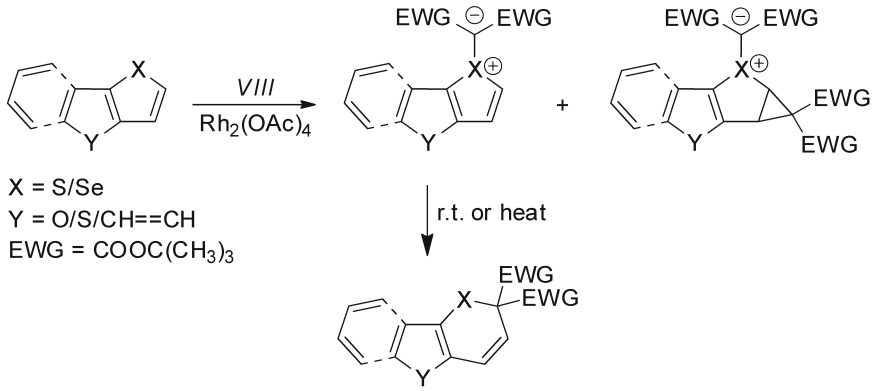

Fig. 2. Outline of the reactivity of thiophenes and thiophenium-ylides.

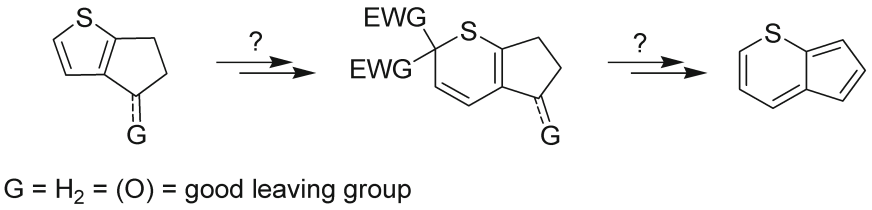

Fig. 3. Desired outcome of the present study.

Experimental

General

All solvents were used as obtained unless otherwise stated. THF and diethyl ether were distilled from sodium benzophenone ketyl; DMF, Et_3N, and pyridine from CaH_2. All other reagents were obtained from commercial sources (Sigma–Aldrich, USA; Lach-Ner, Czech Republic). ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Merkury Plus(Varian, Germany) as solutions in $CDCl_3$ at 25 ℃. Chemical shifts are given in the δ scale. Melting points (uncorrected) were determined using a Leica Galen III melting point apparatus (Wagner & Munz, Germany). Infrared spectra were recorded on a Nicolet 6700 instrument (Thermo Scientific, USA) in $CHCl_3$ solutions and are reported as wave numbers (cm^{-1}). Merck 60 Kieselgel (Merck, Germany) was used for column chromatography. Thin layer chromatography (TLC) was performed on Kieselgel 60 F_{254}-coated aluminum sheets (Merck, Germany).

3-(Thien-2-yl)acrylic acid (II)

A mixture of thiophene-2-carbaldehyde (*I*) (10.17 g, 0.09 mol), malonic acid (20.57 g, 0.2 mol), dry pyridine (80 mL), and piperidine (2 mL) was stirred at 100 ℃ for 4.5 h. Then, the reaction mixture was allowed to cool down and it was poured into 6 M HCl (200 mL). The solid was filtered, washed thoroughly with distilled water (2 × 50 mL) and dried under reduced pressure. The yield of 12.43 g (89 %) of *II*, m.p. 153.2–153.8 ℃ (methanol), was obtained (Ito et al., 1995; m.p. 145–148 ℃).

Methyl 3-(thien-2-yl)propanoate (III)

A sealed tube charged with acid *II* (4.0 g, 0.026 mol), 10% Pd/C (0.4 g) and dry methanol (100 mL) was hydrogenated (pressure of hydrogen = 600 kPa) and stirred at 70 ℃ for 12 h. The catalyst was filtered off, washed with methanol and the combined filtrate was removed under reduced pressure to leave the ester *III* as yellowish oil in the yield of 4.35 g (98 %) (Yuen, 2004).

3-(Thien-2-yl)propanoic acid (IV)

A mixture of ester *III* (3.57 g, 0.02 mol) and sodium hydroxide (4.0 g, 0.10 mol) in water/THF solution (55 mL, φ_r = 10 : 1) was heated to reflux for 3 h. The mixture was then cooled to laboratory temperature and poured into aqueous solution of HCl (10 %, 100 mL). The product was extracted with ether (3 × 30 mL); the combined organic layers were washed with water (10 mL) and brine (2 × 10 mL), dried over $MgSO_4$, and concentrated under reduced pressure to yield 3.1 g (99 %) of acid *IV*, m.p. 46 ℃ (Stuckwisch & Bailey, 1963; m.p. 45–46.5 ℃).

5,6-Dihydrocyclopenta[b]thiophen-4-one (V)

To vigorously stirred polyphosphoric acid (570 g), a solution of acid *IV* (11.4 g, 0.073 mol) in chlorobenzene (290 mL) was added dropwise (during 3 min) at

130 °C in argon atmosphere. After 20 min, the mixture was poured on ice; the organic layer was separated, and the aqueous solution was extracted with 1,2-dichloroethane (5 × 50 mL). The combined organic solution was washed with saturated aqueous solution of $NaHCO_3$ (50 mL) and water (50 mL), and dried with anhydrous $MgSO_4$. The solvent was evaporated and the residue chromatographed (hexane/ethyl acetate, $\varphi_r = 2 : 1$) to yield 3.64 g (36 %) of *V*, m.p. 123–124 °C (Poirier & Lozach, 1966; m.p. 118 °C).

5,6-Dihydro-4H-cyclopenta[b]thiophene (VI)

A mixture of ketone *V* (0.84 g, 6.1 mmol), hydrazine hydrate (1.5 mL, 30 mmol), and diethylene glycol was stirred at 120 °C for 2 h. Then, powdered potassium hydroxide (2.5 g, 45 mmol) was added and the mixture was heated at 200 °C for 4 h. After cooling to laboratory temperature, the mixture was diluted with water (50 mL) and the product was extracted with hexane (3 × 20 mL). The combined organic solution was washed with water (10 mL) and dried with anhydrous $MgSO_4$. After evaporation, the product was purified by column chromatography (hexane) to yield 0.22 g (29 %) of oily *VI*.

5,6-Dihydro-4H-cyclopenta[b]thiophen-4-ol (VIIa)

A mixture of ketone *V* (500 mg, 3.6 mmol), $LiAlH_4$ (70 mg, 1.8 mmol), and dry THF (50 mL) was stirred at room temperature for 1 h in argon atmosphere. The reaction was quenched by a subsequent addition of ethyl acetate (10 mL) and water (10 mL). The mixture was extracted with ethyl acetate (3 × 30 mL); the combined organic solution was washed with water (20 mL) and dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was purified by column chromatography (hexane/ethyl acetate, $\varphi_r = 2 : 1$). The amount of 430 mg (85 %) of *VIIa* was isolated.

4-(tert-Butyldimethylsilyloxy)-5,6-dihydro-4H-cyclopenta[b]thiophene (VIIb)

A solution of *tert*-butyldimethylsilyl chloride (500 mg, 3.3 mmol) in DMF (10 mL) was added dropwise to a solution of *VIIa* (420 mg, 3.0 mmol) in pyridine (5 mL) and DMF (10 mL) during 40 min in argon atmosphere. The mixture was stirred at room temperature for 1 h, diluted with water (100 mL) and extracted with ethyl acetate (3 × 20 mL). The organic solution was washed with water (10 mL) and dried with anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography (hexane/toluene, $\varphi_r = 2 : 1$). to yield 500 mg (66 %) of *VIIb* as yellowish oil.

4-Ethoxy-5,6-dihydro-4H-cyclopenta[b]thiophene (VIIc)

To a solution of *VIIa* (500 mg, 3.6 mmol) in dry THF (10 mL), a 60 % sodium hydride solution in oil (150 mg, 3.6 mmol) was added and after stirring for 5 min also ethyl bromide (0.27 mL, 3.6 mmol) was added. The mixture was stirred at laboratory temperature for 1 h, diluted with water (20 mL), and extracted with ethyl acetate EtOAc (2 × 10 mL). The combined organic solution was washed with water (10 mL) and dried with anhydrous $MgSO_4$. After column chromatography (hexane/ethyl acetate, $\varphi_r = 6 : 1$), 390 mg (65 %) of ether *VIIc* were isolated as yellowish oil.

(5,6-Dihydro-4H-cyclopenta[b]thiophen-4-yl) acetate (VIId)

Acetic anhydride (710 mg, 7 mmol) was added to a solution of *VIIa* (890 mg, 6.3 mmol), DMAP (80 mg, 0.6 mmol), triethylamine (5 mL), and dry dichloromethane (2 mL). The mixture was stirred at room temperature for 1 h, diluted with water (30 mL), and extracted with ethyl acetate (2 × 20 mL). The organic solution was washed with water (10 mL) and dried with anhydrous $MgSO_4$. The solvent was evaporated and the product was purified by column chromatography (hexane/ethyl acetate, $\varphi_r = 6 : 1$). The amount of 460 mg (40 %) of oily ester *VIId* was obtained.

Reaction of VI with diazomalonate di-tert-butyl diazomalonate VIII

A mixture of *VI* (220 mg, 1.8 mmol), diazomalonate *VIII* (640 mg, 2.7 mmol), rhodium acetate (5 mg), and 1,2-dichloroethane (5 mL) was stirred at 80 °C for 15 min. After removing the solvent, the residue was separated by column chromatography (gradient elution with hexane/ethyl acetate, $\varphi_r = 4 : 1$, to chloroform/methanol, $\varphi_r = 9 : 1$). The amount of 20 mg (9 %) of the starting compound *VI* was isolated followed by 20 mg (3 %) of ylide di-*tert*-butyl (5,6-dihydro-1λ^4-4*H*-cyclopenta[*b*]thiophen-1-ylidene)malonate*(IXa)* and 60 mg (10 %) of di-*tert*-butyl 6,7-dihydro-5*H*-cyclopenta[*b*]thiopyran-2,2-dicarboxylate (*Xa*).

Reaction of VIIb with diazomalonate VIII

A mixture of *VIIb* (270 mg, 1.06 mmol), diazomalonate *VIII* (390 mg, 1.6 mmol), and rhodium acetate (5 mg) in 1,2-dichloroethane (5 mL) was stirred at 80 °C for 15 min. The solvent was removed and the residue separated by column chromatography (gradient elution with hexane/ethyl acetate, $\varphi_r = 4 : 1$, to chloroform/methanol, $\varphi_r = 9 : 1$). Up to 200 mg (74 %)

of *VIIb* were recovered along with 1.5 mg (3 %) of ylide di-*tert*-butyl (4-tert-butyldimethylsilyloxy-1λ^4-5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-1-ylidene)malonate *(IXb)* and 55 mg (11 %) of di-*tert*-butyl 5-(tert-butyldimethylsilyloxy)-6,7-dihydro-5*H*-cyclopenta[*b*] thiopyran-2,2-dicarboxylate *(Xb).*

Di-tert-butyl 4-ethoxy-5,6-dihydro-slbf 1λ⁴-4H-cyclopenta[b]thiophen-1-ylidene)malonate (Xc)

A mixture of *VIIc* (230 mg, 1.37 mmol), diazomalonate *VIII* (500 mg, 2 mmol), rhodium acetate (5 mg), and 1,2-dichloroethane (5 mL) was stirred at 80 °C for 15 min. The solvent was evaporated and the residue chromatographed (gradient elution with hexane/ethyl acetate, $\varphi_r = 4:1$, to chloroform/methanol, $\varphi_r = 9:1$). The amount of 50 mg (22 %) of the starting ether *VIIc* and 40 mg (8 %) of product *Xc* were obtained.

Di-tert-butyl 5-acetoxy-6,7-dihydro-5H-cyclopenta[b]thiopyran-2,2-dicarboxylate (Xd)

A mixture of acetate *VIId* (450 mg, 2.44 mmol), diazomalonate *VIII* (890 mg, 3.7 mmol), rhodium acetate (5 mg), and 1,2-dichloroethane (5 mL) was stirred at 80 °C for 15 min. The solvent was evaporated and the residue chromatographed (gradient elution with hexane/ethyl acetate, $\varphi_r = 4:1$, to chloroform/methanol, $\varphi_r = 9:1$) to yield 40 mg (4 %) of ester *Xd* along with 220 mg (49 %) of the starting compound *VIId*.

Results and discussion

To obtain acid *IV*, the Knoevenagel reaction of thiophene-2-carbaldehyde (*I*) and malonic acid was employed in the first step to obtain unsaturated acid *II* (Fig. 4). In the next step, an attempt to obtain acid *IV* by standard hydrogenation of *II* in methanol at slightly elevated temperature. However, during the hydrogenation, the palladium catalyst acted obviously also as a Lewis acid and the saturated ester *III* was isolated in a one pot-procedure in high yield. Subsequent saponification of ester *III* yielded acid *IV* in the overall yield of 86 % in four formal steps. Although 5-exo-trig cyclization is allowed, in this particular case, despite numerous attempts, intramolecular acylation of acid *IV* proceeded only with difficulty and provided low yields. Initial experiments performed using the in situ prepared acid chloride in the presence of various Lewis acids ($SnCl_4$, $TiCl_4$, $AlCl_3$) failed in accordance with literature (Poirier & Lozach, 1966). Moreover, cyclization through the mixed mesyl anhydride (Bonini et al., 2004) and methyl ester *III*, respectively, in the presence of Lewis acids was also unsuccessful. Finally, the reaction of acid *IV* in neat polyphosphoric acid

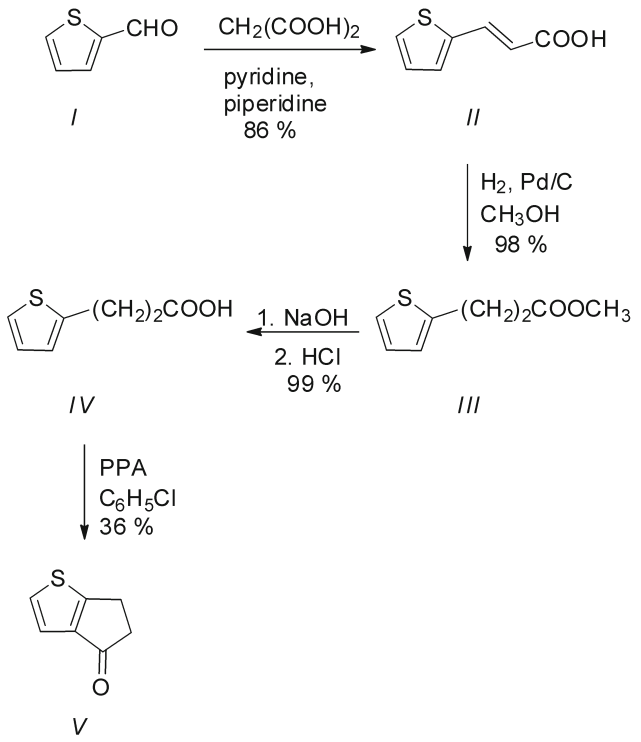

Fig. 4. Synthesis of ketone *V*.

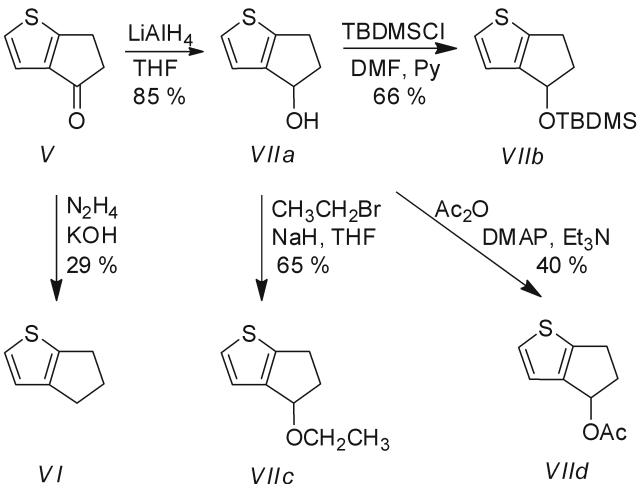

Fig. 5. Synthesis of derivatives *VI* and *VIIa–VIId*.

(PPA) at 100 °C led to the required ketone *V*, albeit in a very low yield (< 10 %). Encouraged by this result, further optimizations of the reaction (concentration of PPA, solvent, reaction temperature, time) were attempted yielding compound *V* in an acceptable 36 % yield, i.e. higher than that previously reported (Sam & Thompson, 1963).

Furthermore, starting with ketone *V*, a short series of derivatives exihibing different steric and electronic effects in the planned transformations (Fig. 5) was prepared. The Wolff–Kishner reduction (Mohamadi et

Table 1. Characterization data of prepared compounds

Compound	Formula	M_r	w_i(calc.)/% w_i(found)/%		Yield	M.p.
			C	H	%	°C
VI	C_7H_8S	124.21	67.69 67.44	6.49 6.52	29	–
VIIa	C_7H_8OS	140.20	59.97 60.12	5.75 4.71	85	90–91
VIIb	$C_{13}H_{22}OSSi$	254.47	61.36 61.15	8.71 8.86	66	–
VIIc	$C_9H_{13}OS$	169.30	63.86 63.92	7.74 7.80	65	–
VIId	$C_9H_{10}O_2S$	182.20	59.32 59.45	5.53 5.59	40	–
IXa	$C_{18}H_{26}O_4S$	338.50	63.88 63.67	7.74 7.89	3	–
Xa	$C_{18}H_{26}O_4S$	338.50	63.88 63.96	7.74 7.66	10	–
Xb	$C_{24}H_{40}O_5SSi$	468.70	61.50 61.30	8.60 8.41	11	–
Xc	$C_{20}H_{32}O_5S$	384.50	62.47 62.58	8.39 8.48	8	–
Xd	$C_{20}H_{28}O_6S$	396.50	60.58 60.65	7.12 7.20	4	–

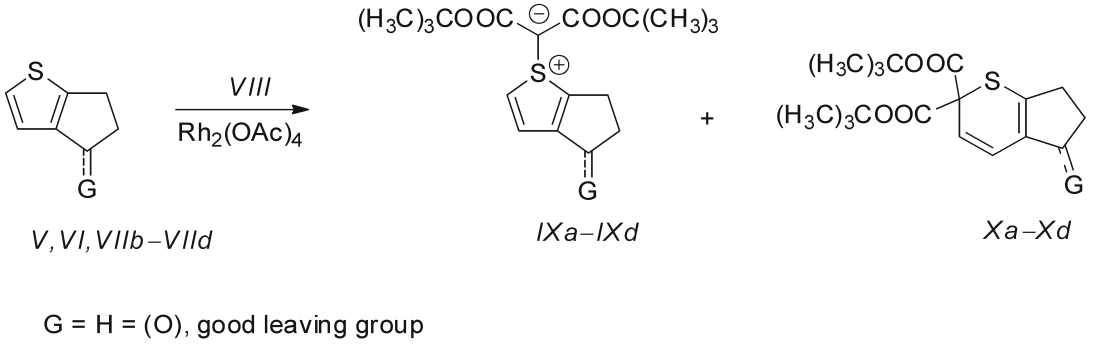

Fig. 6. Reaction of *V*, *VI*, and *VIIb–VIId* with diazomalonate *VIII*.

al., 1992) afforded the parent heterocycle *VI* in a low yield, and the reduction of ketone by $LiAlH_4$ yielded alcohol *VIIa* which was further transformed to the corresponding silyl derivative *VIIb*, ethyl ether *VIIc*, and acetate *VIId* by standard methods.

Based on the previous results (Machara et al., 2009), a smooth addition of rhodium carbenoid generated from *VIII* to the aromatic sulfur resulting in the formation ylide which can undergo a successive rearrangement to the required thialene derivative, even at room temperature, was expected. However, the ylide formation turned out to be the critical step of the planned reaction sequence. The reaction was carried out by heating *VIII* with the corresponding intermediates *V*, *VI*, *VIIb–VIId* in 1,2-dichloroethane for 15 min under argon atmosphere. The formed products were carefully separated by column chromatography, their physico–chemical data are summarized in Table 1, spectral data in Table 2 and yields in Table 3.

Compound *V* did not react with the in situ formed carbenoid which can be explained by the presence of the electron-withdrawing carbonyl group in position 3. A similar phenomenon was observed for a series of various benzothiophenes (Vuorinen et al., 1991). Therefore, the conclusion was drawn that it is easier to obtain the desired intermediate using the parent cyclopentathiophene *VI*. Indeed, the corresponding ylide *IXb* was isolated from a complex mixture along with the thiopyran derivative *Xb* as a result of a spontaneous rearrangement of the formed ylide (Fig. 6). Analogously, for the silyl derivative *VIIb*, both ylide *IXc* and the rearranged product *Xc* were isolated in low yields (3 % and 11 %, respectively). In order to rule out the influence of the steric effect on the course of the reaction, further investigations were carried out with *VIIc* and *VIId*. Reaction of *VIIc* with diazomalonate *VIII* provided ylide *IXd* as the sole product. However, the ylide showed a remarkable stability and

Table 2. Spectral data of prepared compounds

Compound	Spectral data
VI	IR, $\tilde{\nu}$/cm^{-1}: 2924, 2852, 1462, 1377, 804 ^{1}H NMR ($CDCl_3$), δ: 7.19 (d, 1H, $J_{2,3}$ = 4.9 Hz, H-2), 6.84 (d, 1H, H-3), 2.94 (t, 2H, J = 6.9 Hz), 2.74 (t, 2H, J = 6.9 Hz), 2.52 (m, 2H, J = 6.9 Hz) ^{13}C NMR ($CDCl_3$), δ: 146.6, 142.3, 127.5 (CH), 122.2 (CH), 29.7 (CH_2), 28.7 (CH_2), 28.0 (CH_2)
VIIa	IR, $\tilde{\nu}$/cm^{-1}: 3595, 3441, 2970, 2941, 2865, 1456, 1395, 1308, 1044, 944 ^{1}H NMR ($CDCl_3$), δ: 7.20 (d, 1H, $J_{2,3}$ = 4.9 Hz, H-2), 6.95 (d, 1H, H-3), 5.17 (bs, 1H, H-4), 3.08 (m, 1H), 2.88 (m, 1H), 2.81 (m, 1H), 2.34 (m, 1H), 1.81 (bs, 1H, OH) ^{13}C NMR ($CDCl_3$), δ: 148.3, 145.3, 128.7 (CH), 121.3 (CH), 71.6 (CH), 40.3 (CH_2), 26.5 (CH_2)
VIIb	^{1}H NMR ($CDCl_3$), δ: 7.20 (dd, 1H, $J_{2,3}$ = 5.0 Hz, $J_{2,6}$ = 0.6 Hz, H-2), 6.89 (d, 1H, H-3), 5.25 (t, 1H, J = 5.1 Hz, H-4), 3.08 (m, 1H), 2.82 (m, 2H), 2.33 (m, 1H), 0.97 (s, 9H, $C(CH_3)_3$), 0.17 (s, 6H, 2 × CH_3) ^{13}C NMR ($CDCl_3$), δ: 148.1, 144.3, 128.6 (CH), 121.5 (CH), 72.7 (CH), 40.9 (CH_2), 26.7 (CH_2), 25.9, 18.3 (3 × CH_3), –4.51 (2 × CH_3)
VIIc	IR, $\tilde{\nu}$/cm^{-1}: 2971, 2935, 2862, 1440, 1331, 1090, 703 ^{1}H NMR ($CDCl_3$), δ: 7.19 (d, 1H, $J_{2,3}$ = 5.0 Hz, H-2), 6.95 (d, 1H, H-3), 4.86 (dd, 1H, J = 7.0 Hz, J = 3.5 Hz, H-4), 3.58 (q, 2H, J = 7.0 Hz, CH_2), 3.10 (m, 1H), 2.78 (m, 2H), 2.47 (m, 1H), 1.22 (t, 3J = 7.0 Hz, CH_3) ^{13}C NMR ($CDCl_3$), δ: 146.4, 146.1, 128.3 (CH), 122.0 (CH), 78.6 (CH), 63.5 (CH_2), 37.3 (CH_2), 26.8 (CH_2), 15.5 (CH_3)
VIId	IR, $\tilde{\nu}$/cm^{-1}: 2944, 1740 (C═O), 1371, 1247, 1018, 943 ^{1}H NMR ($CDCl_3$), δ: 7.18 (d, 1H, $J_{2,3}$ = 5.0 Hz, H-2), 6.93 (d, 1H, H-3), 5.97 (m, 1H, H-4), 3.18 (m, 1H), 2.84 (m, 2H), 2.46 (m, 1H), 2.03 (s, 3H, CH_3) ^{13}C NMR ($CDCl_3$), δ: 170.7, 147.3, 144.5, 128.7 (CH), 122.3 (CH), 74.1 (CH), 36.8 (CH_2), 26.6 (CH_2), 21.0 (CH_3)
IXa	IR, $\tilde{\nu}$/cm^{-1}: 2967, 2839, 1662, 1607, 1462, 1312, 1271, 1176, 1029, 847 ^{1}H NMR ($CDCl_3$), δ: 6.76 (d, 1H, J = 6.1 Hz), 6.15 (d, 1H, J = 6.1 Hz), 3.15 (m, 2H), 2.63 (m, 2H), 2.47 (m, 2H), 1.44 (s, 18H, 2 × $C(CH_3)_3$) ^{13}C NMR ($CDCl_3$), δ: 165.6 (C═O), 154.2, 136.6, 130.4 (CH), 125.0 (CH), 78.7, 51.2, 30.0 (CH_2), 29.7 (CH_2), 28.2 (CH_2), 27.8 (6 × CH_3)
IXb	IR, $\tilde{\nu}$/cm^{-1}: 2982, 2932, 1725 (C═O), 1707 (C═O), 1631, 1495, 1369, 1326, 1158, 1054, 909, 840 ^{1}H NMR ($CDCl_3$), δ: 7.07 (d, 1H, $J_{2,3}$ = 4.8 Hz), 6.75 (d, 1H, $J_{2,3}$ = 4.8 Hz), 4.76 (m, 1H, J = 7.0 Hz), 2.54 (m, 1H), 2.41 (m, 1H), 2.09 (m, 1H), 1.94 (m, 1H), 1.38 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$), 0.80 (s, 9H, $C(CH_3)_3$), 0.12 (s, 3H, CH_3), 0.10 (s, 3H, CH_3) ^{13}C NMR ($CDCl_3$), δ: 165.2 (C═O), 162.0 (C═O), 154.3, 139.2, 128.6 (CH), 121.6 (CH), 84.0, 82.9, 73.5 (CH), 58.1, 44.4 (CH_2), 39.5 (CH_2), 28.8 (3 × CH_3), 27.8 (3 × CH_3), 25.1 (3 × CH_3), 18.1, –5.0 (CH_3)
Xa	IR, $\tilde{\nu}$/cm^{-1}: 2978, 2934, 1732 (C═O), 1457, 1370, 1258, 1167, 848 ^{1}H NMR ($CDCl_3$), δ: 6.13 (d, 1H, $J_{3,4}$ = 10.2 Hz, H-4), 5.60 (d, 1H, H-3), 2.49 (t, 2H, J = 7.2 Hz, CH_2), 2.42 (t, 2H, J = 7.2 Hz, CH_2), 1.90 (kv, 2H, J = 7.2, CH_2), 1.46 (s, 18H, 2 × $C(CH_3)_3$) ^{13}C NMR ($CDCl_3$), δ: 166.7 (C═O), 128.9, 128.5, 125.8 (CH), 114.4 (CH), 82.8, 44.3, 35.2 (CH_2), 33.4 (CH_2), 27.8 (6 × CH_3), 22.1 (CH_2)
Xb	IR, $\tilde{\nu}$/cm^{-1}: 2982, 2931, 1730 (C═O), 1472, 1371, 1159, 1144, 1046, 909 ^{1}H NMR ($CDCl_3$), δ: 6.20 (d, 1H, $J_{3,4}$ = 10.3 Hz, H-4), 5.66 (d, 1H, H-3), 4.83 (m, 1H, J = 5.2 Hz), 2.59 (m, 1H), 2.39 (m, 1H), 2.32 (m, 1H), 1.73 (m, 1H), 1.45 (s, 9H, $C(CH_3)_3$), 1.44 (s, 9H, $C(CH_3)_3$), 0.87 (s, 9H, $C(CH_3)_3$), 0.07 (s, 3H, CH_3), 0.05 (s, 3H, CH_3) ^{13}C NMR ($CDCl_3$), δ: 166.8 (C═O), 166.4 (C═O), 132.3, 130.8, 124.3 (CH), 114.7 (CH), 83.1, 82.9, 76.9 (CH), 60.8, 33.6 (CH_2), 32.5 (CH_2), 27.6 (9 × CH_3), 25.8 (3 × CH_3), 18.1, –4.2 (CH_3), –4.7 (CH_3)
Xc	IR, $\tilde{\nu}$/cm^{-1}: 2979, 2935, 1744 (C═O), 1630, 1459, 1370, 1255, 1151 ^{1}H NMR ($CDCl_3$), δ: 7.02 (d, 1H, $J_{2,3}$ = 5.5 Hz), 6.81 (d, 1H, $J_{2,3}$ = 5.5 Hz), 4.75 (m, 1H, H-4), 3.54 (m, 2H, J = 7.0 Hz, J = 4.4 Hz, CH_2), 2.78 (m, 2H), 2.69 (m, 1H), 2.38 (m, 1H), 1.39 (s, 18H, 2 × $C(CH_3)_3$), 1.20 (t, 3H, J = 7.0 Hz, CH_3) ^{13}C NMR ($CDCl_3$), δ: 164.8 (2 × C═O), 150.9, 146.4, 128.4 (CH), 122.0 (CH), 79.3, 78.7 (CH), 64.6, 63.6, 37.3 (CH_2), 35.9 (CH_2), 27.6 (6 × CH_3), 15.5 (CH_3)
Xd	IR, $\tilde{\nu}$/cm^{-1}: 2978, 1725, 1370, 1255, 1160, 1058 ^{1}H NMR ($CDCl_3$), δ: 6.30 (d, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 5.68 (dd, 1H, $J_{3,4}$ = 1.2 Hz, H-3), 4.75 (bs, 1H, H-5), 2.64 (m, 1H,), 2.40 (m, 1H), 2.16, (s, 3H, CH_3), 1.78 (m, 1H), 1.45 (s, 18H, 2 × $C(CH_3)_3$ ^{13}C NMR ($CDCl_3$), δ: 170.6 (C═O), 166.8 (2 × C═O), 128.5, 128.0, 125.7 (CH), 114.3 (CH), 83.0, 82.6, 75.5 (CH), 44.3, 35.0 (CH_2), 33.5 (CH_2), 27.8 (3 × CH_3), 27.7 (3 × CH_3), 21.0 (CH_3)

it did not rearrange to the required thialene derivative even at a long-term heating in toluene. On the contrary, the only product isolated from the reaction of thiophene *VIId* was thiopyran *Xd* in a very low yield of 4 %.

The observed low yields of the formed ylides are probably caused by their low thermal stability compared to that of the known substituted thiophenium ylides (Bowles et al., 1988a, 1988b). It can be argued that stability of ylides is sensitive to electronic

Table 3. Yields and recovery of starting material for the reaction with diazomalonate

Starting material	Recovery/%	Products			
		Compound	Yield/%	Compound	Yield/%
VI	9	*IXa*	3	*Xa*	10
VIIb	74	*IXb*	3	*Xb*	11
VIIc	22	*IXc*	8	*Xc*	0
VIId	49	*IXd*	0	*Xd*	4

effects (Porter, 1989) but herein reported findings are not consistent enough for such a general statement. Perhaps the synergic effect of low transformation to the corresponding ylides (Table 3) and their inherent instability which also can lead to undesirable dealkylation to the starting *VIIb*–*VIId* can account for the acquired results. In addition, variable amounts of unidentifiable polymeric by-products of the studied reaction were obtained.

Conclusions

The apparent low stability and the lack of the ability to rearrange to thermodynamically more stable thiopyrans is distinct from the reactivity of fused thiophenium-ylides reported recently. Hence, all studied reactions provided only unsatisfactory yields of the expected thiopyrans, showing that the initial task has to be reconsidered.

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