

PREPARATION AND REACTIONS OF THIENO[3,2-*b*]FURAN DERIVATIVES

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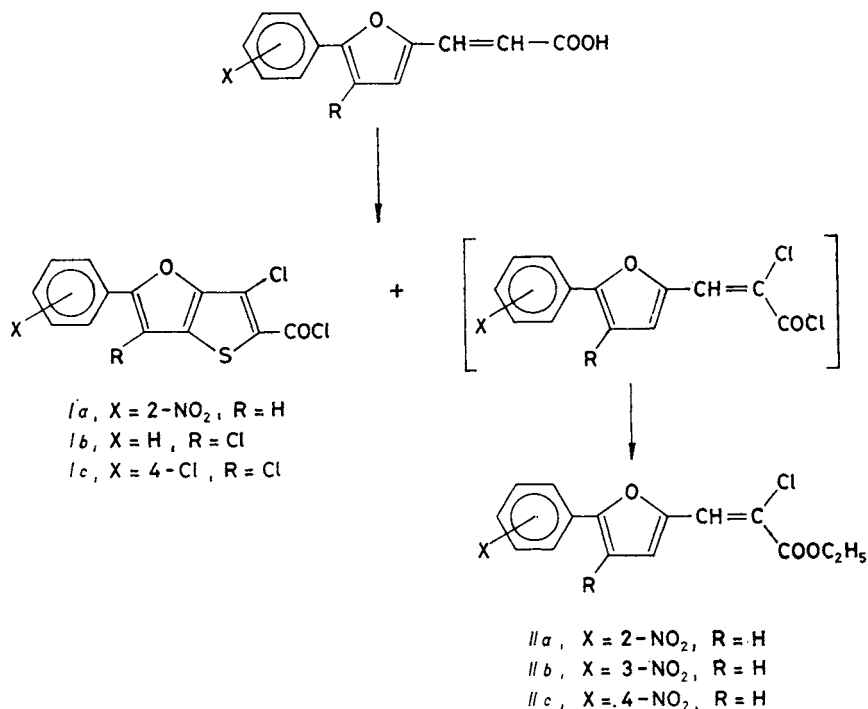
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Reactions of 3-(5-aryl-2-furyl)propenoic, 3-(2-benzo[*b*]furyl)propenoic and 3-(5-ethoxycarbonyl-4*H*-furo[3,2-*b*]-2-pyrrolyl)propenoic acids with thionyl chloride in the presence of triethylbenzylammonium chloride were investigated. The obtained 2-arylthieno[3,2-*b*]furan-5-carboxylic acid chlorides *Ia–Ic* and 3-chlorothieno[3,2-*b*]benzo[*b*]furan-2-carboxylic acid chloride afforded in substitution nucleophilic reactions the corresponding esters *V* and carboxylic acids *VI* which were decarboxylated to *VII*. 3-Chlorothieno[3,2-*b*]benzo[*b*]furan-2-carboxylic acid chloride (*Id*), 6-ethoxycarbonyl-3-chlorothieno[2',3':4,5]furo[3,2-*b*]pyrrole-2-carboxylic acid chloride (*IV*), and ethyl 3-chlorothieno[2',3':4,5]furo[3,2-*b*]indole-2-carboxylate (*VIII*), synthesized under conditions of triethylphosphite reduction from ethyl 6-chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylate (*Va*), are new heterocyclic systems.

Higa and Krubsack¹ were the first who described the preparation of 3-chlorobenzo[*b*]thiophene-2-carboxylic acid by heating 3-phenylpropanoic acid in thionyl chloride in the presence of a catalytic amount of pyridine. This reaction, later studied with derivatives of 3-phenylpropanoic^{2,3}, 3-phenylpropenoic^{2,4,5} acids, 1,1-diphenylalkenes⁶, and derivatives of propionic acid⁷ proved suitable for preparation of many benzo[*b*]thiophene derivatives. This method was utilized in the series of heterocyclic compounds for preparation of thieno[3,2-*b*]thiophenes⁸.

This paper concerns the examination of this reaction with some derivatives of 3-(2-furyl)propenoic acids. 3-[5-(2-Nitrophenyl)-2-furyl]propenoic acid gave on heating in thionyl chloride in the presence of triethylbenzylammonium chloride a substituted thieno[3,2-*b*]furan (*Ia*), and ethyl 2-chloro-3-[5-(2-nitrophenyl)-2-furyl]propenoate (*IIa*) resulting from simmering the oily residue in ethanol (Scheme 1). On the other hand, 3- and 4-nitrophenyl substituted 3-(2-furyl)propenoic acid did not yield thieno[3,2-*b*]furan derivatives at all (monitored by thin-layer chromatography), the reaction mixture furnished after addition of ethanol only ethyl 2-chloro-3-(5-aryl-2-furyl)propenoate with a nitro group in position 3 or 4 of the phenyl ring (*IIb, c*) (Scheme 1). 3-(2-Furyl)propenoic acids containing phenyl and 4-chlorophenyl groups in position 5 of the furan ring afforded, however, thieno[3,2-*b*]furan derivatives of type *I*, but in comparison with *Ia* the chlorine atom enters position 3 (*Ib, c*) (Scheme 1), what is with derivative *Ia* impossible due to steric hindrance associated

with the nitro group in position 2 of the phenyl ring. 3-(2-Benzo[*b*]furyl)propenoic acid yields a product containing thieno[3,2-*b*]benzo[*b*]furan skeleton (*Id*). The hetero skeleton formed from mutually fused furan, pyrrole, and thiophene rings (*IV*) was obtained from 3-(5-ethoxycarbonyl-4*H*-furo[3,2-*b*]-2-pyrrolyl)propenoic acid (*III*) prepared by Knoevenagel condensation of the corresponding aldehyde.

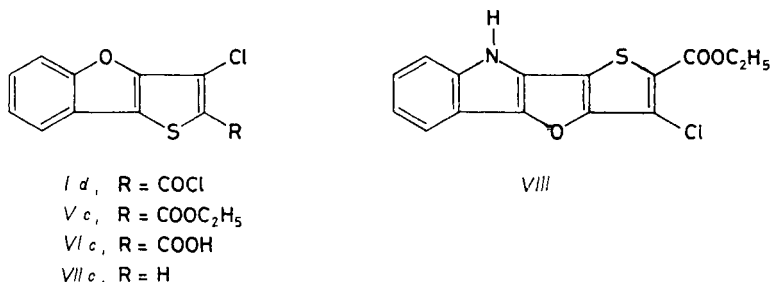


SCHEME 1

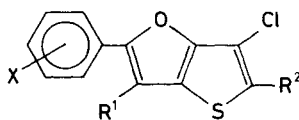
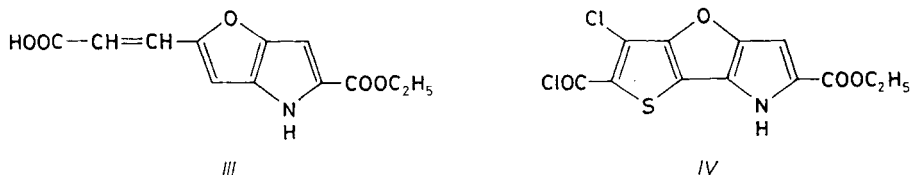
6-Chloro-2-arylthieno[3,2-*b*]furan-5-carboxylic acid chlorides *Ia*–*Ic* and 3-chloro-thieno[3,2-*b*]benzo[*b*]furan-2-carboxylic acid chloride afforded on boiling with ethanol the corresponding esters *Va*–*Vc*; base hydrolysis of these chlorides led to carboxylic acids *VIa*–*VIc* which easily decarboxylated in quinoline under catalysis of copper(II) chromite to *VIIa*–*VIIc*. The presence of nitro group in position 2 of the phenyl ring was utilized with ethyl 6-chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylate (*Va*) to fuse an indole skeleton to thieno[3,2-*b*]furan system *VIII* under conditions of Cadogan^{9,10} deoxygenation.

The most intense band in the electronic spectra of compounds *VIIa*–*VIIc* was found at 289–307 nm. Spectra of compounds *Ia*–*Id*, esters *V* and products of hydrolysis *VI* showed a bathochromic shift by 25 nm due to entering the carbonyl group into conjugation with the thieno[3,2-*b*]furan ring. Compounds containing 2-nitro-

phenyl substituent (*Ia, IIa, V–VIIa*) revealed a hypochromic shift in comparison with the structurally analogous derivatives; this behaviour is caused by deviation of the phenyl ring from the molecule plane and consequently in disconnecting the conjugation due to steric hindrances caused by the nitro group in position 2 of the phenyl ring. Most remarkable was the phenomenon manifested with compounds *IIa–IIc*, where the difference between λ_{\max} of 2-nitrophenyl and 4-nitrophenyl derivatives was found to be 43 nm.



Wavenumbers characterizing the carbonyl vibrations of acid chlorides *Ia–Id* occurred at 1707–1752 cm⁻¹, those of esters *Va–Vc* and carboxylic acids *VIa* to *VIc* at 1699–1701 and 1645–1665 cm⁻¹, respectively. Nitrophenyl derivatives *Ia, IIa–IIc, V–VIIa* displayed adsorption of nitro group at 1527–1501 cm⁻¹ ($\nu_{\text{as}}(\text{NO}_2)$) and 1352–1326 cm⁻¹ ($\nu_{\text{s}}(\text{NO}_2)$).



- Va*, X = 2-NO₂; R¹ = H; R² = COOC₂H₅
Vb, X = H; R¹ = Cl; R² = COOC₂H₅
VIa, X = 2-NO₂; R¹ = H; R² = COOH
VIb, X = H; R¹ = Cl; R² = COOH
VIc, X = 4-Cl; R¹ = Cl; R² = COOH
VIIa, X = 2-NO₂; R¹ = H; R² = H
VIIb, X = H; R¹ = Cl; R² = H

Mass spectrum of compounds *Ia*, *b* revealed only little intense peaks of molecular radical ions which are accompanied by isotopic ions $[M + 2]^{+\bullet}$; the $M^{+\bullet}$ to $[M + 2]^{+\bullet}$ ratio corresponded to two (*Ia*) or three (*Ib*) atoms of chlorine in the molecule. The molecular radical ion of compound *VIII* showed a 100% relative intensity, this being in favour of its high stability.

EXPERIMENTAL

6-Chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylic Acid Chloride (*Ia*)

A mixture of 3-[5-(2-nitrophenyl)-2-furyl]propenoic acid (2.59 g, 10 mmol) and triethylbenzylammonium chloride (2.27 g, 10 mmol) was heated in thionyl chloride (3.57 g, 30 mmol) at 140°C. An additional portion of thionyl chloride (5.95 g, 50 mmol) was gradually added and the mixture was stirred for 2 h. The excess of thionyl chloride was distilled off, and the solid residue was extracted with benzene. The combined benzene extracts were washed with water and dried with sodium sulfate. The solvent was partly removed and the precipitated product was filtered off. Yield 0.6 g (17.5%), m.p. 206°C (benzene). For $C_{13}H_5Cl_2NO_4S$ (342.2) calculated: 45.63% C, 1.47% H, 20.73% Cl, 4.09% N, 9.37% S; found: 45.21% C, 1.39% H, 20.86% Cl, 3.98% N, 9.49% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 707 (C=O), 1 501 (NO₂)_{as}, 1 326 (NO₂)_s, UV spectrum, λ_{\max} , nm (log ϵ , $m^2 mol^{-1}$): 319 (3.04). ¹H NMR spectrum ((C²H₅)₂SO, δ , ppm): 7.45 (1 H, s, C₍₃₎-H), 8.04–7.62 (m, 4 H, H_{arom}). Mass spectrum, m/z (relat. intens., %): 343 (9), 341 (16), 308 (32), 306 (80.6), 271 (38), 269 (56.4), 262 (64), 234 (77), 206 (77), 169 (97), 145 (100), 130 (22.6), 104 (40), 76 (81). This procedure was employed for preparation of compounds *Ib*–*Id* and *IV*. Ethyl 2-chloro-3-[5-(2-nitrophenyl)-2-furyl]propenoate (*Ila*) was obtained from the oily residue gained after removing the solvent by heating in ethanol (30 ml) for 20 min. Yield 0.2 g (6.2%), m.p. 86°C (ethanol). For $C_{15}H_{12}ClNO_5$ (321.7) calculated: 55.60% C, 3.76% H, 11.02% Cl, 4.35% N; found: 55.42% C, 3.58% H, 11.38% Cl, 4.21% N. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 703 (C=O), 1 515 (NO₂)_{as}, 1 327 (NO₂)_s. UV spectrum, λ_{\max} , nm (log ϵ , $m^2 mol^{-1}$): 399 (3.55). ¹H NMR spectrum (C²HCl₃, δ , ppm): 7.81 (s, 1 H, H_A), 7.34 (d, 1 H, C₍₄₎-H), 6.82 (d, 1 H, C₍₃₎-H), 4.35 (q, 2 H, CH₂), 1.36 (t, 3 H, CH₃), 7.88–7.45 (m, 4 H, H_{arom}), $J_{3,4} = 3.9$. Mass spectrum, m/z (relat. inters., %): 323 (12), 321 (36), 276 (12), 256 (12), 221 (14.5), 188 (29), 170 (27.4), 161 (48), 139 (48), 133 (100), 116 (42), 104 (42), 77 (52).

3,6-Dichloro-2-phenylthieno[3,2-*b*]furan-5-carboxylic acid chloride (*Ib*), yield 13%, m.p. 201°C (benzene). For $C_{13}H_5Cl_3O_2S$ (331.6) calculated: 47.09% C, 1.52% H, 32.08% Cl, 9.67% S; found: 46.82% C, 1.49% H, 32.21% Cl, 9.81% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 721 (C=O). UV spectrum, λ_{\max} , nm (log ϵ , $m^2 mol^{-1}$): 336 (3.36). ¹H NMR spectrum ((C²H₅)₂SO, δ , ppm): 7.91–7.38 (5 H, m, H_{arom}). Mass spectrum, m/z (relat. intens., %): 336 (7), 332 (32), 330 (32), 297 (71), 295 (100), 269 (7), 267 (10), 241 (10), 239 (17), 145 (21), 105 (45), 77 (34).

3,6-Dichloro-2-(4-chlorophenyl)thieno[3,2-*b*]furan-5-carboxylic acid chloride (*Ic*), yield 8%, m.p. 204°C (benzene). For $C_{13}H_4Cl_4O_2S$ (366.1) calculated: 42.65% C, 1.10% H, 38.74% Cl, 8.76% S; found: 42.13% C, 1.08% H, 39.01% Cl, 8.64% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 732 (C=O). UV spectrum, λ_{\max} , nm (log ϵ , $m^2 mol^{-1}$): 340 (3.46). ¹H NMR spectrum ((C²H₅)₂SO, δ , ppm): 7.85; 7.51 (dd, 4 H, H_{arom}).

3-Chlorothieno[3,2-*b*]benzo[*b*]furan-2-carboxylic acid chloride (*Id*), yield 21%, m.p. 183°C (benzene). For $C_{11}H_4Cl_2O_2S$ (271.1) calculated: 48.73% C, 1.49% H, 26.15% Cl, 11.83% S; found: 48.17% C, 1.44% H, 25.91% Cl, 11.67% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 752 (C=O).

UV spectrum, λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 323 (3.47). ^1H NMR spectrum ($(\text{C}^2\text{H}_5)_2\text{SO}$, δ , ppm): 8.06–7.25 (m, 4 H, H_{arom}).

Ethyl 2-chloro-3-[5-(3-nitrophenyl)-2-furyl]propenoate (IIb), yield 18%, m.p. 148°C (ethanol). For $\text{C}_{15}\text{H}_{12}\text{ClNO}_5$ (321.7) calculated: 55.60% C, 3.76% H, 11.02% Cl, 4.35% N; found: 55.49% C, 3.58% H, 10.97% Cl, 4.12% N. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 687 (C=O), 1 527 (NO_2)_s, 1 329 (NO_2)_s. UV spectrum, λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 350 (3.54). ^1H NMR spectrum (C^2HCl_3 , δ , ppm): 7.86 (s, 1 H, H_A), 7.35 (d, 1 H, $\text{C}_{(4)}\text{-H}$), 6.98 (d, 1 H, $\text{C}_{(3)}\text{-H}$), 4.38 (q, 2 H, CH_2), 1.39 (t, 3 H, CH_3), 8.51 (s, 1 H, H_{arom}), 8.25–7.69 (m, 3 H, H_{arom}).

Ethyl 2-chloro-3-[5-(4-nitrophenyl)-2-furyl]propenoate (IIc), yield 27%, m.p. 142°C (ethanol). For $\text{C}_{15}\text{H}_{12}\text{ClNO}_5$ (321.7) calculated: 55.60% C, 3.76% H, 11.02% Cl, 4.35% N; found: 55.16% C, 3.49% H, 10.84% Cl, 4.17% N. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 699 (C=O), 1 503 (NO_2)_{as}, 1 326 (NO_2)_s. UV spectrum, λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 382 (3.57). ^1H NMR spectrum ($(\text{C}^2\text{H}_5)_2\text{SO}$, δ , ppm): 7.80 (s, 1 H, H_A), 7.45 (d, 1 H, $\text{C}_{(3)}\text{-H}$), 7.41 (d, 1 H, $\text{C}_{(4)}\text{-H}$), 4.21 (q, 2 H, CH_2), 1.23 (t, 3 H, CH_3), 8.23, 7.98 (dd, 4 H, H_{arom}).

3-(5-Ethoxycarbonyl-4H-furo[3,2-*b*]-2-pyrrolyl)propenoic Acid (III)

To a solution of malonic acid (5.7 g, 55 mmol) in pyridine (9 ml) ethyl 2-formyl-4H-furo[3,2-*b*]pyrrole-5-carboxylate¹¹ (10.35 g, 50 mmol) and piperidine (0.4 g) were added. The mixture was heated at 90°C for 8 h, poured on hydrochloric acid acidified crushed ice and the precipitate was filtered off. Yield 9.5 g (65.7%), m.p. 245°C (ethanol). For $\text{C}_{12}\text{H}_{11}\text{NO}_5$ (249.2) calculated: 57.83% C, 4.45% H, 5.62% N; found: 57.55% C, 4.31% H, 5.49% N. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 601 (C=O), 1 668 (C=O). UV spectrum, λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 351 (3.67). ^1H NMR spectrum ($(\text{C}^2\text{H}_5)_2\text{SO}$, δ , ppm): 7.32 (d, 1 H, H_A), 6.93 (d, 1 H, $\text{C}_{(6)}\text{-H}$), 6.63 (d, 1 H, $\text{C}_{(3)}\text{-H}$), 6.15 (d, 1 H, H_B), 4.21 (q, 2 H, CH_2), 1.23 (t, 3 H, CH_3), $J_{A,B} = 16$, $J_{3,6} = 0.8$ Hz.

*6-Ethoxycarbonyl-3-chlorothieno[2',3':4,5]furo[3,2-*b*]pyrrole-2-carboxylic acid chloride* (IV) was obtained from III in 14% yield, m.p. 263°C (benzene). For $\text{C}_{12}\text{H}_7\text{Cl}_2\text{NO}_4\text{S}$ (332.2) calculated: 43.39% C, 2.12% H, 21.35% Cl, 4.21% N, 9.65% S; found: 43.28% C, 2.08% H, 21.42% Cl, 4.11% N, 9.53% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 736 (C=O), 1 669 (C=O). UV spectrum, λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 250 (2.98). ^1H NMR spectrum ($(\text{C}^2\text{H}_5)_2\text{SO}$, δ , ppm): 7.28 (s, 1 H, $\text{C}_{(5)}\text{-H}$), 4.35 (q, 2 H, CH_2), 1.28 (t, 3 H, CH_3).

Ethyl 6-Chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylate (Va)

6-Chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylic acid chloride (3.42 g, 10 mmol) was refluxed in ethanol for 30 min, the solvent was distilled off and the crude product was crystallized. Yield 3.4 g (97%), m.p. 136°C (ethanol). For $\text{C}_{15}\text{H}_{10}\text{ClNO}_5\text{S}$ (351.8) calculated: 51.20% C, 2.87% H, 10.08% Cl, 3.98% N, 9.11% S; found: 50.96% C, 2.63% H, 9.94% Cl, 3.66% N, 9.03% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 699 (C=O), 1 522 (NO_2)_{as}, 1 342 (NO_2)_s. UV spectrum, λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 319 (3.26). ^1H NMR spectrum (C^2HCl_3 , δ , ppm): 6.98 (s, 1 H, $\text{C}_{(3)}\text{-H}$), 4.40 (q, 2 H, CH_2), 1.40 (t, 3 H, CH_3), 7.90–7.59 (m, 4 H, H_{arom}). This procedure was employed for preparation of compounds *Vb, c*.

*Ethyl 3,6-dichloro-2-phenylthieno[3,2-*b*]furan-5-carboxylate* (Vb), yield 97%, m.p. 131°C (ethanol). For $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{O}_3\text{S}$ (341.2) calculated: 52.80% C, 2.95% H, 20.78% Cl, 9.40% S; found: 52.59% C, 2.73% H, 20.58% Cl, 9.26% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 701 (C=O). UV spectrum, ν_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 336 (3.46). ^1H NMR spectrum (C^2HCl_3 , δ , ppm): 4.40 (q, 2 H, CH_2), 1.39 (t, 3 H, CH_3), 8.09–7.44 (m, 5 H, H_{arom}).

*Ethyl 3-chlorothieno[3,2-*b*]benzo[*b*]furan-2-carboxylate (Vc)*, yield 97%, m.p. 102°C (ethanol). For $C_{13}H_9ClO_3S$ (280.7) calculated: 55.62% C, 3.23% H, 12.63% Cl, 11.42% S; found: 55.37% C, 3.19% H, 12.58% Cl, 11.31% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 701 (C=O). UV spectrum, λ_{\max} , nm ($\log \epsilon$, $m^2 mol^{-1}$): 322 (3.33). 1H NMR spectrum ($(C^2H_3)_2SO$, δ , ppm): 4.28 (q, 2 H, $C_{(2)}$), 1.27 (t, 3 H, CH_3), 8.06–7.25 (m, 4 H, H_{arom}).

6-Chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylic Acid (VIa)

A solution of NaOH (30%, 60 ml) was added to 6-chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylic acid chloride dissolved in ethanol (200 ml) and the mixture was refluxed for 2 h. Hydrochloric acid was added to the hot solution and the obtained precipitate was filtered off. Yield 2.2 g (68.1%), m.p. 254°C (ethyl acetate). For $C_{13}H_6ClNO_5S$ (323.7) calculated: 48.23% C, 1.87% H, 10.95% Cl, 4.33% N, 9.90% S; found: 48.08% C, 1.59% H, 10.84% Cl, 4.21% N, 9.83% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 658 (C=O), 1 506 (NO_2)_{as}, 1 352 (NO_2)_s. UV spectrum, λ_{\max} , nm ($\log \epsilon$, $m^2 mol^{-1}$): 313 (3.16). 1H NMR spectrum ($(C^2H_3)_2SO$, δ , ppm): 7.43 (s, 1 H, $C_{(3)}$ -H), 8.04–7.62 (m, 4 H, H_{arom}). According to this procedure compounds *Vb*–*Vd* were synthesized.

*3,6-Dichloro-2-phenylthieno[3,2-*b*]furan-5-carboxylic acid (VIb)*, yield 64%, m.p. 280°C (ethyl acetate). For $C_{13}H_6Cl_2O_3S$ (313.2) calculated: 49.86% C, 1.93% H, 22.64% Cl, 10.24% S; found: 49.66% C, 1.79% H, 22.37% Cl, 10.32% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 645 (C=O). UV spectrum, λ_{\max} , nm ($\log \epsilon$, $m^2 mol^{-1}$): 338 (3.12). 1H NMR spectrum ($(C^2H_3)_2SO$, δ , ppm): 7.93–7.43 (m, 5 H, H_{arom}).

*3-Chlorothieno[3,2-*b*]benzo[*b*]furan-5-carboxylic acid (VIc)*, yield 69%, m.p. 312°C (ethyl acetate). For $C_{11}H_5ClO_3S$ (252.7) calculated: 52.29% C, 1.99% H, 14.03% Cl, 12.69% S; found: 52.17% C, 1.83% H, 13.78% Cl, 12.76% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 665 (C=O). UV spectrum, λ_{\max} , nm ($\log \epsilon$, $m^2 mol^{-1}$): 313 (3.33). 1H NMR spectrum ($(C^2H_3)_2SO$, δ , ppm): 8.08–7.33 (m, 4 H, H_{arom}).

*3,6-Dichloro-2-(4-chlorophenyl)thieno[3,2-*b*]furan-5-carboxylic acid (VI_d)*, yield 61%, m.p. 289°C (ethyl acetate). For $C_{13}H_5Cl_3O_3S$ (347.6) calculated: 44.92% C, 1.45% H, 30.60% Cl, 9.22% S; found: 44.73% C, 1.38% H, 30.42% Cl, 9.17% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 645 (C=O). UV spectrum, λ_{\max} , nm ($\log \epsilon$, $m^2 mol^{-1}$): 341 (3.38). 1H NMR spectrum ($(C^2H_3)_2SO$, δ , ppm): 7.51, 7.58 (dd, 4 H, H_{arom}).

4-Chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan (VIIa)

The stirred solution consisting of 6-chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylic acid (3.24 g, 10 mmol) and copper(II) chromate (0.64 g) in quinoline (20 ml) was reacted at 190°C under nitrogen for 2 h, cooled and poured into ether (300 ml). The ethereal solution was washed with dilute hydrochloric acid (0.1 mol l^{-1}) to neutral reaction, dried with sodium sulfate, the solvent was distilled off and the product was crystallized. Yield 0.64 g (23%), m.p. 112°C (hexane). For $C_{12}H_6ClNO_3S$ (279.7) calculated: 51.53% C, 2.16% H, 12.68% Cl, 5.00% N, 11.46% S; found: 51.37% C, 2.08% H, 12.49% Cl, 4.88% N, 11.43% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 509 (NO_2)_{as}, 1 352 (NO_2)_s, 1 352 (NO_2)_s. UV spectrum, λ_{\max} , nm ($\log \epsilon$, $m^2 mol^{-1}$): 239 (3.10). 1H NMR spectrum ($(C^2H_3)_2SO$, δ , ppm): 7.60 (s, 1 H, $C_{(5)}$ -H), 7.39 (s, 1 H, $C_{(3)}$ -H), 8.00–7.59 (m, 4 H, H_{arom}). Compounds *VIIb,c* were also prepared according to this procedure.

*3,6-Dichloro-2-phenylthieno[3,2-*b*]furan (VIIb)*, yield 27%, m.p. 70°C (hexane). For $C_{12}H_6Cl_2OS$ (269.2) calculated: 53.55% C, 2.25% H, 26.35% Cl, 11.91% S; found: 53.25% C, 2.17% H,

26.21% Cl, 11.79% S. UV spectrum λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 307 (3.28). ^1H NMR spectrum ($(\text{C}^2\text{H}_3)_2\text{SO}$, δ , ppm): 7.68 (s, 1 H, $\text{C}_{(5)}\text{-H}$), 7.93–7.38 (m, 5 H, H_{arom}).

3-Chlorothieno[3,2-*b*]benzo[*b*]furan (VIIc), yield 31%, m.p. 67°C (hexane). For $\text{C}_{10}\text{H}_5\text{ClOS}$ (224.7) calculated: 53.46% C, 2.24% H, 15.78% Cl, 14.27% S; found: 53.26% C, 2.18% H, 15.54% Cl, 14.35% S. UV spectrum, λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 283 (3.07), 290 (3.06), 302 (3.85). ^1H NMR spectrum ($(\text{C}^2\text{H}_3)_2\text{SO}$, δ , ppm): 7.15 (s, 1 H, $\text{C}_{(2)}\text{-H}$), 7.71–7.17 (m, 4 H, H_{arom}).

Ethyl 3-Chlorothieno[2',3' - 4,5]furo[3,2-*b*]indole-2-carboxylate (VIII)

Ethyl 6-chloro-2-(2-nitrophenyl)thieno[3,2-*b*]furan-5-carboxylate (3.51 g, 10 mmol) was refluxed in triethylphosphite (20 g) in a nitrogen atmosphere for 4 h, the mixture was cooled and the precipitated product was filtered off. Yield 84%, m.p. 274°C (ethanol). For $\text{C}_{15}\text{H}_{10}\text{ClNO}_3\text{S}$ (319.8) calculated: 56.34% C, 3.15% H, 11.09% Cl, 4.38% N, 10.03% S; found: 56.15% C, 3.07% H, 10.89% Cl, 4.29% N, 10.21% S. IR spectrum (KBr) ν_{\max} , cm^{-1} : 1 679 (C=O). UV spectrum, λ_{\max} , nm ($\log \epsilon$, $\text{m}^2 \text{mol}^{-1}$): 370 (4.77). Mass spectrum, m/z (relat. intens., %): 321 (39), 319 (100), 293 (39), 291 (100), 274 (16), 247 (42), 211 (26), 183 (35), 139 (16), 105.5 (16), 78 (55), 76 (22).

Spectral Measurements

The IR spectra were measured with a Specord 71 IR (Zeiss, Jena) spectrophotometer, the electronic spectra of methanolic solutions (concentration $3 \cdot 10^{-5}$ – $8 \cdot 10^{-5} \text{ mol l}^{-1}$) were recorded with a Specord UV VIS (Zeiss, Jena) apparatus, the ^1H NMR spectra were run with a BS 487 C (Tesla, Brno) spectrometer operating at 80 MHz; tetramethylsilane and hexamethyldisiloxane were the internal references for C^2HCl_3 and $(\text{C}^2\text{H}_3)_2\text{SO}$ solvents, respectively. The mass spectra were recorded with a MS 902 S (AEI, Manchester) instrument at 70 eV electron energy and 100 μA trap current.

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