

Abderrahim Jilale, Pierre Netchitaïlo* and Bernard Decroix

Laboratoire de Chimie, UER des Sciences et des
Techniques de l'Université du Havre, 30 rue Gabriel Péri,
76600 Le Havre, France

Daniel Vegh

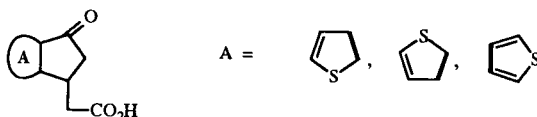
Department of Organic Chemistry, Slovak Technical University,
81237 Bratislava, Czechoslovakia
Received February 1, 1993

Oxidihydrocyclopentathiophenacetic acids **4**, **5** and **6** were synthesized from suitable 2- or 3-formylthiophenes. Reactivity of the carbonyl group or the carboxylic group of these bicyclic systems was investigated. The Beckmann rearrangement of methyl 6-oximino-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-4-acetate **12** is an interesting route to methyl 7-oxo-4,5,6,7-tetrahydrothieno[2,3-*c*]pyridin-4-acetate (**13**).

J. Heterocyclic Chem., **30**, 881 (1993).

Some derivatives from cyclopenta[*b*]thiophenecarboxylic acids show analgesic and antiinflammatory activities [1,2]. In this connection, we have investigated the synthesis of thiophene analogs with the following structures.

Scheme I



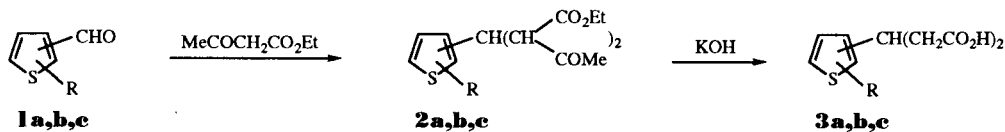
Thienylglutaric acids **3** were synthesized in two steps by condensation of ethyl acetoacetate with 2-formyl-**1a**, 3-formyl-**1b**, and 3-formyl-2-methylthiophenes **1c** followed by treatment with potassium hydroxide.

Acid derivatives **3a,b,c** were cyclized using polyphosphoric acid (PPA) or 10% phosphorus pentoxide in methanesulfonic acid (Method A) or a Friedel-Crafts reaction (Method B). Reactions with PPA were associated with serious resinification and low yield (10 to 30%). Methanesulfonic acid allowed us to decrease reaction time and working temperature. Under these conditions, compound

5 was obtained. However, the cyclization reaction was not complete with thienylglutaric acids **3a** and **3c**. Compounds **4** and **6** were synthesized using a Friedel-Crafts reaction. We tested aluminium chloride and stannic chloride as Lewis acids. Higher yields were obtained with aluminium chloride, in contrast to the results reported by Cagniant on the synthesis of methylcyclopentathiophenones [3]. As expected, cyclization with the 3 or 4 position of the thiophene ring was more difficult and was coupled with poor yields or incomplete reactions. The ¹H nmr analysis of compounds **4** and **5** showed that they present an AB thiophene system and an ABX cyclopentane system. The latter was composed of two well resolved doublets of doublets (H_{5a}-H_{5b}). The two protons H₅ were coupled as gem protons (J_{5a-5b} = 17.5 Hz). In addition, H_{5a} and H_{5b} were coupled with H₄ (J_{4-5a} = 7.6 Hz, J_{4-5b} = 4.4 Hz). The higher coupling constant was attributed to H₅ in the *cis* position as described in cyclopentane systems [4].

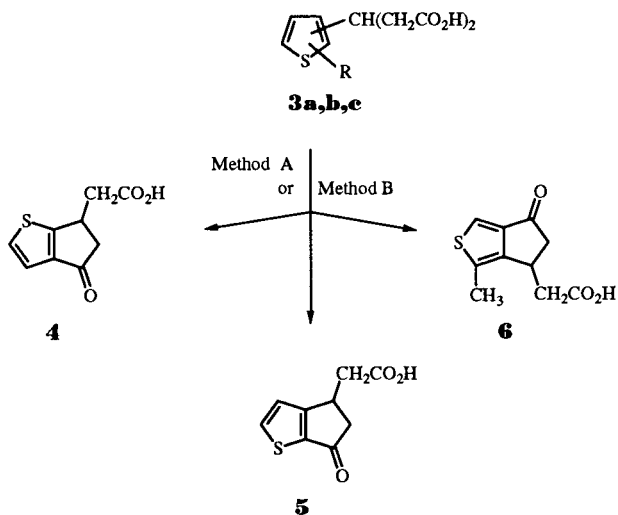
Reactivity of the carbonyl and carboxylic groups was investigated in compounds **4** and **5**. An acid solution of **5** in anhydrous methanol afforded the ester derivative **7**. However, under the same conditions the acid **4** led to a mixture

Scheme II



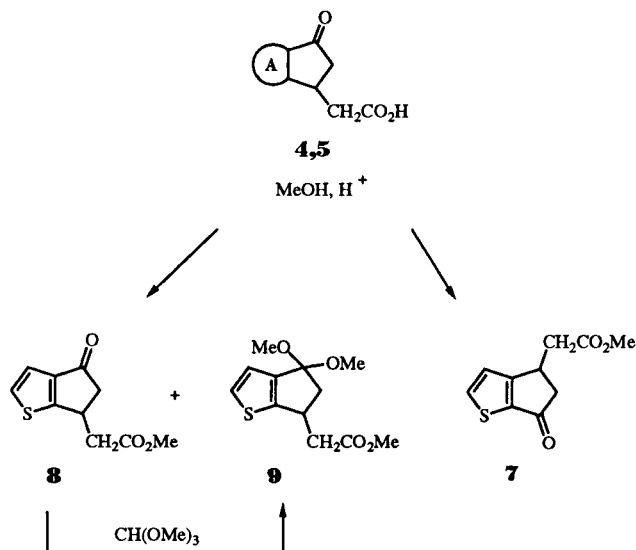
Product	Position	a	b	c
1	2	CHO	H	CH ₃
	3	H	CHO	CHO
2	2	CH(CH(Ac)CO ₂ Et) ₂	H	CH ₃
	3	H	CH(CH(Ac)CO ₂ Et) ₂	CH(CH(Ac)CO ₂ Et) ₂
3	2	CH(CH ₂ CO ₂ H) ₂	H	CH ₃
	3	H	CH(CH ₂ CO ₂ H) ₂	CH(CH ₂ CO ₂ H) ₂

Scheme III



of the ester **8** and ketal **9** derivatives. The ketal **9** was identified by treatment of **8** with methyl orthoformate.

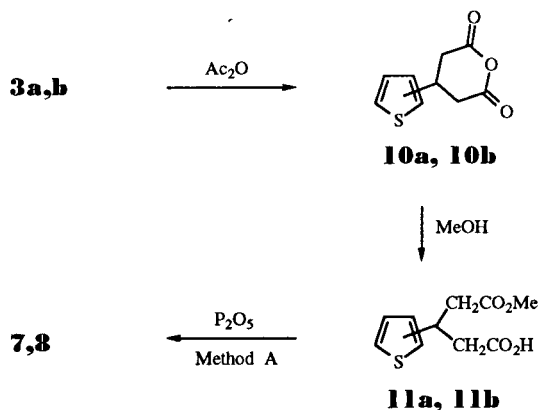
Scheme IV



Anhydride derivatives **10a** and **10b** from **3a** and **3b** were heated in methanol to give acid ester derivatives **11a** and **11b**, respectively. Then, they were cyclized with 10% phosphorus pentoxide in methanesulfonic acid (Method A) as described with thienylglutaric acid **3b**.

The ^1H nmr spectral data for keto esters **7** and **8** are similar to those of keto acids **4** and **5**. Several reactions have been investigated using keto acid **5** or keto ester **7** as starting materials. Cyclopenta[*b*]thiophen-7-one **7** was treated with hydroxylamine hydrochloride to afford a mixture of two oximes **12a** and **12b** in unequal amounts which were separated by liquid chromatography. The two isomers were differentiated by nmr spectroscopy since H_2 of

Scheme V



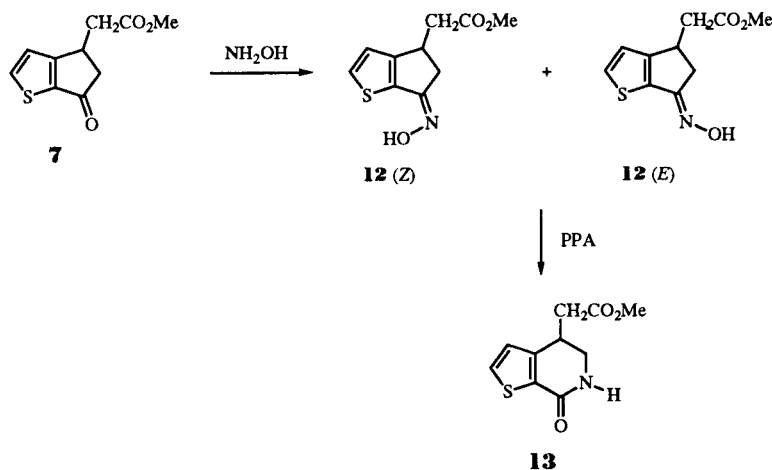
the *Z* form was shifted downfield ($\delta = 7.60$ ppm) compared to that of the *E*-form. The fact that the *Z*-configuration represents the more stable isomer could be explained by interaction between the oxime function and the sulfur atom, which forms a stable six membered chelate as previously described [5]. Treatment of a mixture of two isomers or *Z*-isomer alone by PPA gave a product *via* Beckmann rearrangement, the thienopyridone **13**. In the nmr spectroscopy the two protons of the methoxycarbonylmethyl group are not equivalent. The two H_5 protons were coupled as gem protons. A coupling constant of 3.5 Hz between H_6 (NH) and H_5 support the structure of **13**. This rearrangement process is similar to that reported by Barbry *et al.*, [6] who described the formation of an isoquinolone from cyclopenta[*f*]benzoxazole. It is interesting to note that the *E*-isomer, when treated under the same conditions, led to unchanged starting material.

The carbamate **14** was synthesized by successive treatment of **5** with triethylamine, ethyl chloroformate and sodium azide followed by heating the azide intermediate in methanol. In addition, action of dicyclohexylcarbodi-

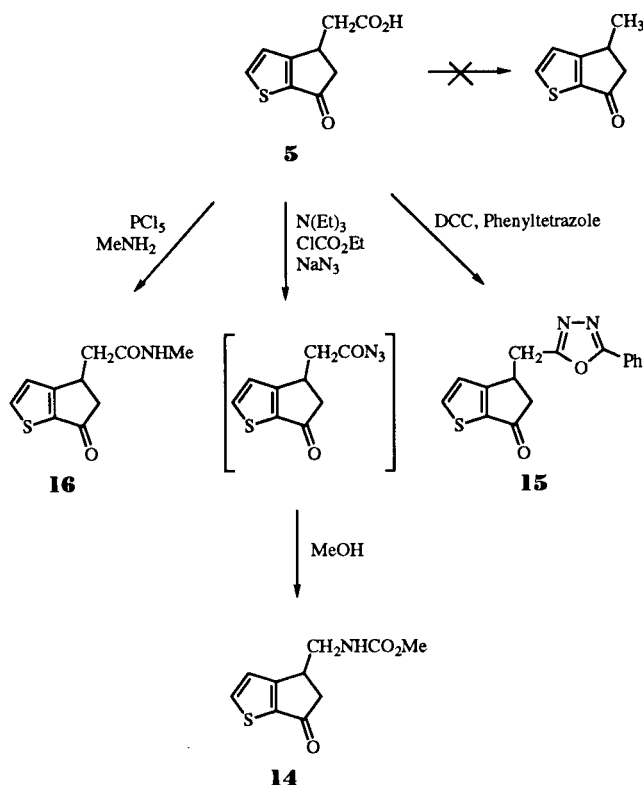
Table 1
Physical and Chemical Data for Compounds **2** and **3**

Compounds No.	Mp (°C)	Yield %	Formula	Analysis	
				Calcd./C%	Found H%
2a	110	70	$\text{C}_{17}\text{H}_{22}\text{O}_6\text{S}$	57.61	6.21
				57.50	6.12
2b	152	75	$\text{C}_{17}\text{H}_{22}\text{O}_6\text{S}$	57.61	6.21
				57.59	6.22
2c	102	50	$\text{C}_{18}\text{H}_{24}\text{O}_6\text{S}$	58.67	6.52
3a	128	50	$\text{C}_9\text{H}_{10}\text{O}_4\text{S}$	50.45	4.70
				50.32	4.67
3b	148	52	$\text{C}_9\text{H}_{10}\text{O}_4\text{S}$	50.45	4.70
				50.55	4.46
3c	144	41	$\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}$	52.61	5.30
				53.01	5.46

Scheme VI



Scheme VII



imide and phenyltetrazole gave the oxadiazole **15** as described by Povazanec *et al.* [7]. The amide derivative **16** was obtained from **5** and a mixture of phosphorus pentachloride and methylamine.

Finally, **5** was not decarboxylated to give 4-methyl-6-oxo-4,5-dihydro-6H-cyclopenta[b]thiophene as previously described [8].

Table 2

 $^1\text{H-NMR}$ Spectral Data for Compounds **2** and **3**

Compound No.	δ ppm
2a	2.7 (4H, m, 2CH_2), 3.56 (3H, s, OCH_3), 6.86 (2H, m, $\text{H}_3\text{-H}_5$), 7.16 (1H, t, $J = 3.1$ Hz, H_4)
2b	2.65 (4H, m, 2CH_2), 3.60 (3H, s, OCH_3), 6.95 (1H, q, $J = 1.2$ Hz, $J = 5$ Hz, H_4), 7.10 (1H, q, $J = 1.2$ Hz, $J = 3$ Hz, H_2), 7.25 (1H, q, $J = 3$ Hz, $J = 5$ Hz, H_5)
2c	2.26 (3H, s, CH_3), 3.55 (3H, s, OCH_3), 6.89 (1H, d, $J = 5$ Hz, H_4), 7.12 (1H, d, $J = 5$ Hz, H_5)
3a	2.50 (4H, d, $J = 6.5$ Hz, 2CH_2), 3.50 (1H, m, CH), 6.89 (2H, m, $\text{H}_3\text{-H}_5$), 7.26 (1H, t, $J = 3.1$ Hz, H_4)
3b	2.55 (4H, d, $J = 6.5$ Hz, 2CH_2), 3.40 (1H, m, CH), 7 (1H, q, $J = 1.2$ Hz, $J = 5$ Hz, H_4), 7.16 (1H, q, $J = 1.2$ Hz, $J = 3$ Hz, H_2), 7.33 (1H, q, $J = 3$ Hz, $J = 5$ Hz, H_5)
3c	2.25 (3H, s, CH_3), 2.5 (4H, $J = 6.5$ Hz, 2CH_2), 3.45 (1H, m, CH), 6.89 (1H, d, $J = 5$ Hz, H_4), 7.10 (1H, d, $J = 5$ Hz, H_2)

EXPERIMENTAL

Melting points were taken on a hot-stage apparatus, elemental analyses were obtained in the microanalysis laboratory of the Institut National des Sciences Appliquées, Rouen. The ^1H nmr spectra were recorded on a Bruker AC200 instrument in deuteriochloroform solution and chemical shifts (δ) are expressed in ppm relative to internal hexamethyldisiloxane. Infrared spectra were measured with a Beckman IR 20 spectrophotometer.

General Procedure for the Synthesis of Compound **2**.

Piperidine (2 g) was added in small portions to a stirred mixture of formylthiophene derivatives **1** (150 mmoles) and ethyl acetate (39 g, 300 mmoles) at 0° . The solution was stirred for 2 hours at 0° and then overnight at room temperature. The solid residue was collected by filtration, washed with a minimum amount of cold ether and recrystallized from ethanol. Physical and spectral data of these compounds are listed in Tables 1 and 2.

General Procedure for Thienylglutaric Acids **3a**, **3b** and **3c** Synthesis.

A solution of **2** (7 g) in 5 ml of 7*M* potassium hydroxide was heated at 90° during 30 minutes. The mixture was cooled, poured on to 20 g of ice and washed with ether. The aqueous layer was acidified with 1*M* hydrochloric acid to give a white solid which was recrystallized from ethyl acetate-hexane (80:20 v/v). Physical and spectra data of these compounds are listed in Tables 1 and 2.

Cyclization of Thienylglutaric Acids **3**. General Methods for Ketoacids **4**, **5**, **6** Synthesis.

Method A.

Thienylglutaric acid **3b** (1 g, 4.7 mmoles) was quickly added to a hot solution of 10% phosphorus pentoxide in methanesulfonic acid (20 g). The mixture was vigorously stirred at 100° during 20 minutes. The dark solution was cooled, hydrolyzed with ice and extracted with ether. The organic layers were dried over magnesium sulfate and then concentrated, to give compound **5**.

Method B.

Thienylglutaric acids **3a** and **3c** (10 mmoles) in dichloromethane were refluxed for 3 hours with an excess of thionyl chloride. Then, the chilled solution was treated in portions over 2 hours with aluminium chloride (4 g, 31 mmoles) at 0° with vigorous stirring. The mixture was allowed to react for 1 hour with cooling and for 2 hours at room temperature. After cooling, the mixture was quenched by cautious addition of ice and then diluted with water. The phases were separated and the aqueous phase was extracted with dichloromethane. The combined organic phase was washed with water, dried over magnesium sulfate, filtered and then concentrated to give crude ketones **4** and **6**.

4-Oxo-5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-6-acetic Acid (**4**).

Recrystallization from benzene-hexane (80:20 v/v) gave **4** (60%), mp 75°; ir (potassium bromide): ν 1700 (acid, C=O), 1660 cm^{-1} (ketone, C=O); ¹H nmr: 2.60 (m, 2H, CH₂CO₂H), 2.75 (dd, 1H, J = 4.4 Hz, J = 17.5 Hz, H_s), 3.10 (dd, 1H, J = 7.6 Hz, J = 17.5 Hz, H_s), 3.80 (m, 1H, H₄), 7.15 (d, 1H, J = 5 Hz, H₃), 7.55 (d, 1H, J = 5 Hz, H₂).

Anal. Calcd. for C₉H₈O₃S: C, 55.09; H, 4.10. Found: C, 55.10; H, 4.20.

6-Oxo-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-4-acetic Acid (**5**).

Recrystallization from benzene afforded **5** (70%) as a white solid, mp 130°; ir (potassium bromide): ν 1730 (acid, C=O), 1660 cm^{-1} (ketone, C=O); ¹H nmr: 3.00 (m, 2H, CH₂CO₂H), 3.20 (dd, 1H, J = 4.4 Hz, J = 17.5 Hz, H_s), 3.60 (dd, 1H, J = 7.6 Hz, J = 17.5 Hz, H_s), 4.15 (m, 1H, H₄), 7.70 (d, 1H, J = 5 Hz, H₃), 8.60 (d, 1H, J = 5 Hz, H₂).

Anal. Calcd. for C₉H₈O₃S: C, 55.09; H, 4.10. Found: C, 55.10; H, 4.40.

1-Methyl-4-oxo-5,6-dihydro-4*H*-cyclopenta[*c*]thiophen-6-acetic Acid (**6**).

Recrystallization from benzene gave **6** (40%) as a yellow solid, mp 110°; ir (potassium bromide): ν 1700 (acid, C=O), 1680 cm^{-1} (ketone, C=O); ¹H nmr: 2.33 (s, 3H, CH₃), 2.40 (m, 2H, CH₂CO₂H), 2.60 (dd, 1H, J = 4.6 Hz, J = 17.5 Hz, H₄), 3.00 (dd, 1H, J = 7.5 Hz, J = 17.5 Hz, H₃), 3.36 (m, 1H, H₅), 7.76 (s, 1H,

H₂).

Anal. Calcd. for C₁₀H₁₀O₃S: C, 57.12; H, 4.79. Found: C, 57.01; H, 5.06.

Methyl 6-Oxo-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-4-acetate (**7**).

Direct Esterification.

Keto acid **5** (1.5 g, 7.6 mmoles) was esterified in methanol (50 ml) containing 0.5 ml of concentrated sulfuric acid. The mixture was heated overnight, poured into ice-cold water and extracted with ether to give an oil which was purified by liquid chromatography using silica gel and benzene as eluent. The desired compound **7** was isolated pure (1.1 g, 70%).

Cyclization of **11b**.

Thienylglutaric acid **3b** (5 g, 23.4 mmoles) was refluxed in acetic anhydride (50 ml, 530 mmoles) for 2 hours. After evaporation of the solvent the solid was recrystallized from benzene to give [thien-3-yl]-2-glutaric anhydride **10b** as white crystals (3.6 g, 90%), mp 108°.

Anal. Calcd. for C₉H₈O₃S: C, 55.09; H, 4.11. Found: C, 55.30; H, 4.28.

Anhydride **10b** (2 g) in methanol (50 ml) was heated for 30 minutes. The solvent was evaporated and the ester **11b** was treated without further purification by 10% phosphorus pentoxide in methanesulfonic acid (20 g) for 10 minutes at room temperature and for 20 minutes at 60°. The mixture was poured in 100 ml of ice-water mixture and extracted with ether. The extracts were dried over magnesium sulfate and evaporated. After treatment of the residue as above, pure **7** (80%) was obtained, mp 65°; ¹H nmr: 2.60 (m, 2H, CH₂CO₂CH₃), 2.75 (dd, 1H, J = 4.4 Hz, J = 17.5 Hz, H_s), 3.10 (dd, 1H, J = 7.6 Hz, J = 17.5 Hz, H_s), 3.60 (m, 1H, H₄), 3.85 (s, 3H, OCH₃), 7.10 (d, 1H, J = 5 Hz, H₃), 7.90 (d, 1H, J = 5 Hz, H₂).

Anal. Calcd. for C₁₀H₁₀O₃S: C, 57.12; H, 4.79. Found: C, 56.91; H, 4.48.

Methyl 4-Oxo-5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-6-acetate (**8**).

Direct Esterification.

Using conditions described above for preparation of **7**, acid **4** led to a mixture of keto ester **8** and ketal ester **9** which were not separated by liquid chromatography.

Cyclization of **11a**.

Thienylglutaric acid **3a** treated as **3b** led to the anhydride **10a** as white crystals (75% yield), mp 93°.

Anal. Calcd. for C₉H₈O₃S: C, 55.09; H, 4.11. Found: C, 55.17; H, 4.02.

Compound **8** was prepared by the same method as mentioned above for compound **7** (70% yield); ¹H nmr: 2.60 (m, 2H, CH₂CO₂CH₃), 2.75 (dd, 1H, J = 4.4 Hz, J = 17.5 Hz, H_s), 3.25 (dd, 1H, J = 7.6 Hz, J = 17.5 Hz, H_s), 3.60 (m, 1H, H₄), 3.65 (s, 3H, OCH₃), 6.90 (d, 1H, J = 5 Hz, H₃), 7.50 (d, 1H, J = 5 Hz, H₂).

Anal. Calcd. for C₁₀H₁₀O₃S: C, 57.12; H, 4.79. Found: C, 56.85; H, 4.52.

Methyl 4,4-Dimethoxy-5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-6-acetate (**9**).

A mixture of **8** (1 g, 4.35 mmoles) and catalytic amount of *p*-toluenesulfonic acid in an excess of methyl orthoformate (10 ml) was stirred at room temperature for 70 hours. The solvent was evaporated and the residue was purified by silica gel chromatography

using benzene as eluent to give an oil (0.65 g, 60% yield); ^1H nmr: 2.50-2.70 (m, 2H, $\text{CH}_2\text{-CO}$), 2.95 (dd, 1H, $J = 4.4$ Hz, $J = 17.5$ Hz, H_5), 3.15 (dd, 1H, $J = 7.6$ Hz, $J = 17.5$ Hz, H_3), 3.50 (m, 1H, H_4), 3.65 (s, 3H, CO_2CH_3), 3.80 (s, 6H, OCH_3), 7.00 (d, 1H, $J = 5$ Hz, H_3), 7.60 (s, 1H, $J = 5$ Hz, H_2).

Methyl 6-Oximino-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-4-acetate (**12**).

A mixture of **7** (2.75 g, 14 mmoles), hydroxylamine hydrochloride (1.1 g, 16 mmoles) and sodium acetate (1.33 g, 16 mmoles) in 20 ml of ethanol and 5 ml of water was refluxed for 4 hours. After cooling and addition of 50 ml of water, the solution was extracted with ether. The extracts were dried over magnesium sulfate and concentrated to give an oil (2.2 g, 70% yield) which was purified by silica gel chromatography using benzene-ethyl acetate (80:20 v/v) as eluent to give 60% *Z*-isomer and 40% *E*-isomer; ir (potassium bromide): ν 3400-3300 (O-H), 1720 (C=O), 1640 cm^{-1} (C=N).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_3\text{S}$: C, 53.32; H, 4.88; N, 6.21. Found: C, 53.60; H, 5.05; N, 5.95.

Compound (*Z*)-**12** had mp 78°; ^1H nmr: 2.70 (s, 2H, $\text{CH}_2\text{-CO}$), 2.85 (dd, 1H, $J = 4.5$ Hz, $J = 17.8$ Hz, H_5), 3.40 (dd, 1H, $J = 7.65$ Hz, $J = 17.5$ Hz, H_3), 3.75 (s, 3H, OCH_3), 3.80 (m, 1H, H_4), 6.90 (d, 1H, $J = 5$ Hz, H_3), 7.60 (d, 1H, $J = 5$ Hz, H_2).

Compound (*E*)-**12** was an oily compound; ^1H nmr: 2.70 (m, 3H, $\text{CH}_2\text{-CO}$ and H_5), 3.40 (dd, 1H, $J = 7.65$ Hz, $J = 17.5$ Hz, H_3), 3.75 (s, 3H, OCH_3), 3.80 (m, 1H, H_4), 6.80 (d, 1H, $J = 5$ Hz, H_3), 7.25 (d, 1H, $J = 5$ Hz, H_2).

Methyl 7-Oxo-4,5,6,7-tetrahydrothieno[2,3-*c*]pyridin-4-acetate (**13**).

A mixture of oxime **12** (1 g, 44 mmoles) and polyphosphoric acid (4 g) in 20 ml of xylene was refluxed with vigorous stirring. After evaporation of the solvent, water was added to the residue and the aqueous mixture was neutralized and extracted with chloroform. The extracts were dried over magnesium sulfate and evaporated. The residue was chromatographed using dichloromethane-acetone (9:1 v/v) as the eluant (0.45 g, 45% yield), mp 88°; ir potassium bromide: ν 3250 (N-H), 1720 (ester, C=O), 1650 cm^{-1} (ketone, C=O); ^1H nmr: 2.70 (d, 2H, $J = 7$ Hz, CH_2CO), 3.50 (m, 1H, $J = 3.5$ Hz, $J = 12.8$ Hz, H_5), 3.65 (m, 1H, $J = 3.5$ Hz, H_3), 3.70 (s, 3H, OCH_3), 3.80 (m, 1H, H_4), 7.00 (d, 1H, $J = 5$ Hz, H_3), 7.25 (m, 1H, N-H), 7.55 (d, 1H, $J = 5$ Hz, H_2).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_3\text{S}$: C, 53.32; H, 4.88; N, 6.21. Found: C, 53.20; H, 4.75; N, 6.05.

4-(Methoxycarbonylaminoethyl)-6-oxo-4,5-dihydro-6*H*-cyclopenta[*b*]thiophene (**14**).

The azide derivative was prepared from **5** as described elsewhere [9] and used without further purification. The residue was dissolved in anhydrous benzene and refluxed during 5 hours. The ir spectrum of the mixture showed a characteristic band of

the isocyanate function at 2240 cm^{-1} . Benzene was evaporated and the residue was heated in anhydrous methanol overnight. After evaporation of the solvent, the residue was recrystallized in methanol (60% yield), mp 87°; ir (potassium bromide): ν 3350 (N-H), 1700 cm^{-1} (C=O); ^1H nmr: 2.60-3.60 (m, 5H, $\text{CH}_2\text{-NH}$, H_4 and H_5), 3.70 (s, 3H, CH_3), 4.10 (m, 1H, N-H), 7.15 (d, 1H, $J = 5$ Hz, H_3), 7.95 (d, 1H, $J = 5$ Hz, H_2).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_3\text{S}$: C, 53.32; H, 4.86; N, 6.21. Found: C, 53.50; H, 4.50; N, 6.50.

6-Oxo-4-(5'-phenyl-1',3',4'-oxadiazol-2'-yl)methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophene (**15**).

Compound **5** (0.5 g, 3 mmoles) was added to 0.37 g (3 mmoles) of phenyltetrazole in 10 ml of xylene. The mixture was refluxed for 30 minutes and filtered. After evaporation of the solvent the residue was recrystallized from methanol (0.53 g, 60% yield), mp 115°; ^1H nmr: 1.60-4.30 (m, 5H, CH_2 , H_4 and H_5), 7.15 (d, 1H, $J = 5$ Hz, H_3), 7.45-8.30 (d, 6H, 5H benzene and H_2).

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 64.84; H, 4.08; N, 9.45. Found: C, 64.70; H, 3.78; N, 9.50.

6-Oxo-*N*-methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-4-acetamide (**16**).

A mixture of **5** (2 g, 10 mmoles) and phosphorus pentachloride (2.66 g, 15 mmoles) in 20 ml of methylene chloride was stirred 30 minutes at room temperature. After addition of an excess of anhydrous methylamine (1 g), the mixture was stirred overnight at the same temperature. The solid was filtered off and then recrystallized from ethyl acetate-hexane (1 g, 50% yield), mp 105°; ^1H nmr ($\text{DMSO-}d_6$): 2.30-4.00 (m, 5H, $\text{CH}_2\text{-CO}$, H_4 and H_5), 3.30 (s, 3H, N- CH_3), 4.30 (m, 1H, N-H), 7.15 (d, 1H, $J = 5$ Hz, H_3), 7.90 (d, 1H, $J = 5$ Hz, H_2).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_2\text{S}$: C, 57.39; H, 5.30; N, 6.69. Found: C, 57.09; H, 5.55; N, 6.55.

REFERENCES AND NOTES

- [1] G. Ferrand, J. Barbanton and J. C. Depin, French Patent, 1986, 2,567,125; *Chem. Abstr.*, **105**, 172281 (1986).
- [2] A. E. Jacobson and M. Mokotoff, *J. Med. Chem.*, **13**, 7 (1970).
- [3] G. Cagniant, G. Merle and D. Cagniant, *Bull. Soc. Chim. France*, 325 (1970).
- [4] J. M. Jackman and S. Sternhell, in "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd Ed, Pergamon Press, Oxford, 1969.
- [5] S. Marchalin, B. Decroix and J. Morel, *Acta. Chem. Scand.*, (in press).
- [6] D. Barbry, D. Couturier, N. Abdellatif, D. Lesieur and C. Lespagnol, *J. Heterocyclic Chem.*, **28**, 449 (1991).
- [7] F. Povazanec, J. Kovac and J. Svoboda, *Collect. Czech. Chem. Commun.*, **45**, 1299 (1980).
- [8] S. Gronowitz, P. Moses, A. B. Hornfeldt and F. Hakansson, *Ark. Kem.*, **17**, 165 (1961).
- [9] A. Jilale, B. Decroix and J. Morel, *Chem. Scripta.*, **27**, 423 (1987).