Tetrahedron Vol. 49, No. 30, pp. 6591-6604, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00
Pergamon Press Ltd

On the Syntheses and Photochemical Properties of Novel Pyrrolizinone Derivatives as Photosensitizers

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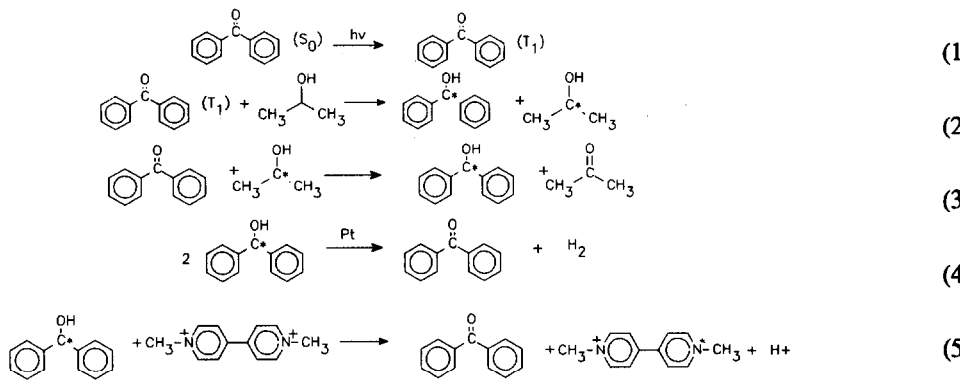
(*Received in Germany* 5 *January* 1993)

Abstract : The syntheses of the pyrrolizinone derivatives 8H-6-methyl-7-phenylthieno[2,3-b]-pyrrolizin-8-one (1), *10H-6,7,8,9-tetrahydro(1)benzothieno[2,3-b]pyrrolizin-10-one* (2), *8H-6-phenylthieno[2,3-b]pyrrolizin-8-one* (3), *8H-methylthieno[2,3-b]pyrrolizin-8-one* (4), *are described. In contrast to benzophenone, compounds* 1 - 4 *absorb in the visible light region* ($\epsilon^{436\ nm}$ = *400, 420, 450, and 320 l* mol^{-1} cm^{-1} *for compounds* 1 - 4, *respectively). 9-Fluorenone as well as compounds* 1 - 4 *were able to reduce methylviologen in the presence of 2-propanol under irradiation with UV light* (λ > 280 *nm). Compounds* 1 - 4 *showed an interesting fluorescence behavior depending on solvent and on Ph - value, which will be discussed in detail.*

INTRODUCTION

Different approaches for the conversion and storage of solar energy have been made by several authors[1-10]. Beside semiconductors[11-12] the use of light absorbing compounds i.e. sensitizers in combination with several catalysts has attracted much attention as basic compounds for conversion of light energy[1-16]. Necessary demands for a useful sensitizer can be described as follows : strong absorption and sufficient long lifetimes of the excited states in order to make charge (energy) transfer reactions possible. Beside organometallic complexes[15,16] like $Ru(bpy)_3Cl_2$ also ketones like benzophenone or fluorenone[13,14] have been investigated as photosensitizers. For example benzophenone is able to reduce 1,1'-dimethyl-4,4'-bipyridinium chloride (= methylviologen = MV^{2+}) via a radical mechanism in the presence of 2-propanol upon irradiation with UV-light to give blue radicals[13]:



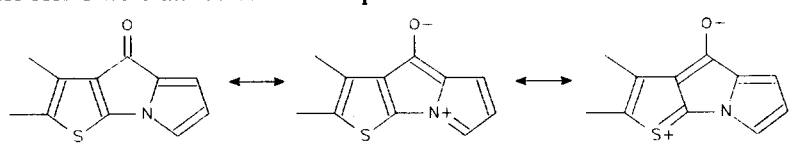
Scheme 1.

Addition of heterogenous catalysts such as platinum or palladium to such solutions led to the formation of hydrogen (4) even in the absence of methyl viologen[14]. Methyl viologen enlarges quantum yields (5). Since benzophenone did not absorb in the visible region, its use for practical applications for the storage of solar light is extremely limited. It was our aim to find fluorenone analogues with stronger absorptions in the visible.

RESULTS AND DISCUSSION

1. *UV/VIS - Spectroscopy.* The UV / VIS spectra for compounds **1 - 4** are shown in Fig.1. In 2-propanol compound **2** gave two absorption maxima at 289 and 325 nm (see TABLE I), while compound **4** showed two maxima at 274 and 320 nm. This bathochromic shift can be attributed to hyperconjugation effects of alkyl substituents. Comparing the absorption properties of compound **3** with compound **4** (see Fig.1), a bathochromic shift of maxima can be observed with compound **3**, which can be explained by the enlargement of the conjugated system.

In contrast to benzophenone, compounds **1 - 4** had absorption maxima at 330 nm (ϵ_{max} : see TABLE I). The higher absorption coefficients of compounds **1 - 4** in the visible light region in contrast to 9-fluorenone can be attributed to the zwitter ionic mesomeric structures[18] of compounds **1 - 4** (see Scheme 2) These mesomeric forms were attributed to be responsible for the absorbance at 450 nm.



Scheme 2. Zwitter ionic structures of compounds **1 - 4.**

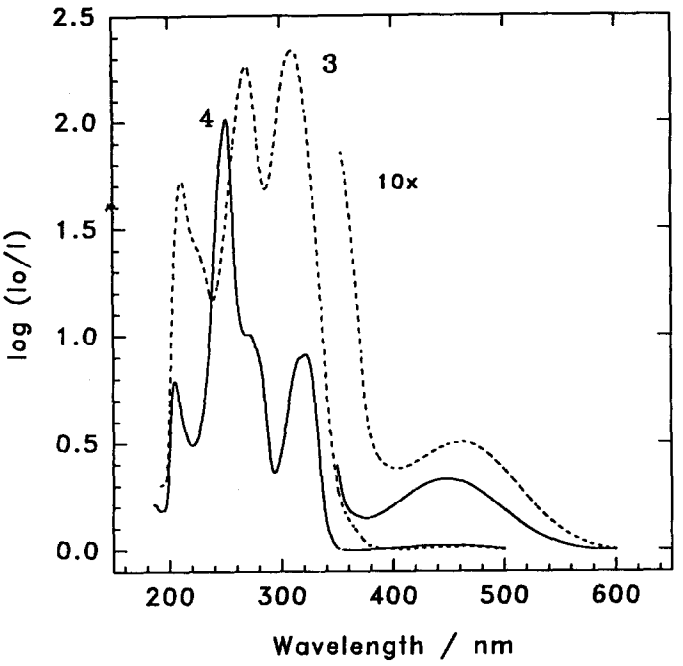


Fig.1 UV /VIS absorption spectra of compounds **3** - **4**.

TABLE I. UV Data (200 - 350 nm) of compounds **1** - **4**.

sensitizer compound	solution	ϵ [l mol^{-1} cm^{-1}] at the maximum (nm)			
bezophenone	[1,A]	(207) 15500	(257) 16500		(325) 1000
fluorenone	[5,A]	(205) 11000	(255) 25000	(298) 2000	(330) 1800
1	[6,A]	(204) 16000	(242) 20000	(280) 8000	(331) 6500
	[4,A]	(210) 19600	(242) 25500	(280) 11600	(333) 8300
2	[4,A]	(204) 11500	(248) 14000	(289) 8610	(320) 6360
	[2,A]	(204) 11500	(250) 20000	(289) 11500	(325) 10000
3	[3,A]	(204) 16300		(273) 21000	(310) 17500
	[2,A]	(210) 17300		(270) 22600	(310) 23300
4	[3,A]	(204) 11500	(250) 21200	(276) 12000	(325) 11000
	[2,A]	(205) 8000	(250) 20000	(274) 10000	(320) 9000

[1] water, [2] 2-propanol, [3] 2-propanol : water = 2 : 3, [4] 2-propanol : water = 3 : 2, [5] 2-propanol : water = 4 : 1, [6] propanol, [7] methanol, [A] c = 10^{-3} mol/l, [B] c = $7x10^{-4}$ mol/l

Furthermore absorption spectra of compounds **1** - **4** were found to depend on pH and solvent. Alkaline solutions of compounds **1** - **4** showed higher absorptions in the visible light region at about 400 nm due to different contributions of zwitter ionic mesomeric forms (e.g. compound **3** see Fig.2):

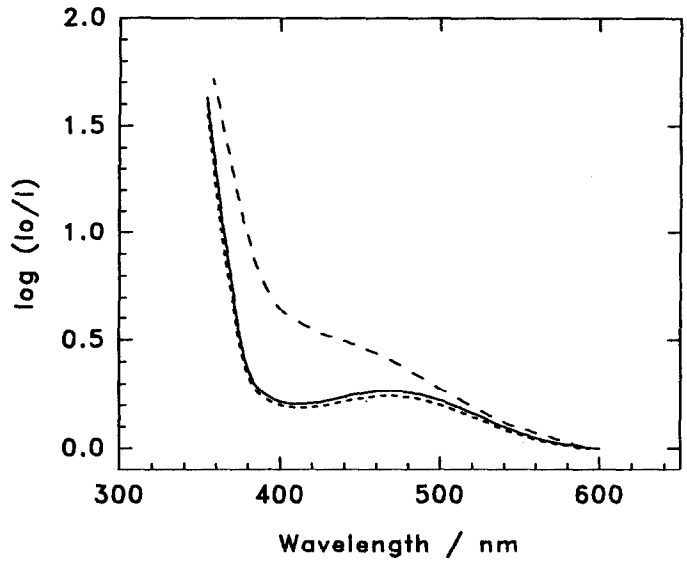


Fig.2 UV/VIS absorption spectra of compound **3** at different pH values (—— : pH = 2, - - - pH = 5.5, — — — : pH = 12).

TABLE II. UV / visible data of compounds **1** - **4** (350 - 500 nm)

sensitizer compound	solution	ϵ [l mol^{-1} cm^{-1}] at the maximum (nm)	436 nm
1	[6,C]	(450) 420	400
	[4,A]	(460) 480	410
2	[4,A]	(420) 400	390
	[2,A]	(458) 460	420
3	[3,A]	(466) 420	370
	[2,A]	(460) 500	450
4	[3,A]	(448) 352	337
	[2,A]	(450) 350	320

[2] 2-propanol, [3] 2-propanol : water = 2 : 3, [4] 2-propanol : water = 3 : 2, [5] 2-propanol: water = 4 : 1, [6] propanol, [7] methanol, [A] c = 10^{-3} mol/l, [B] c = 7.10^{-4} mol/l, [C] c = 5.10^{-3} mol/l

UV spectra of compounds **1** - **4** were quite similar in different solvents, but visible spectra (λ > 350 nm) showed higher absorption coefficients in alcoholic solutions (2-propanol) then in aqueous solutions for compounds **2** and **3** (see Table II).

2. *Fluorescence properties.* Exciting alcoholic solutions (2-propanol / water 3 : 2) of compound **2** with λ^{EX} = 375 nm, fluorescence light can be observed with its maximum at λ^{EM} = 439 nm (and 2 shoulders at 520 and 560 nm). Monitoring the fluorescence intensity at λ^{EM} = 440 nm, and scanning the exciting light from 200 to 420 nm, one maximum of excitation was found at 375 nm :

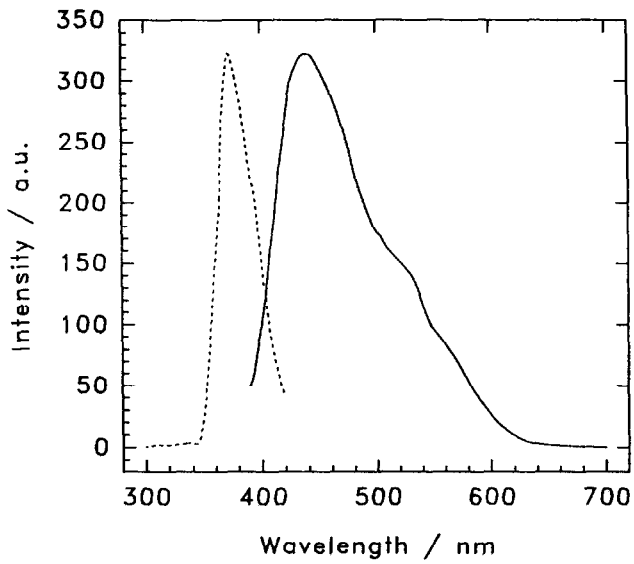


Fig.3 Fluorescence- (———, λ^{EX} = 375 nm) and excitation spectra (- - -, λ^{EM} = 439 nm) of compound **2** in water / 2-propanol 2 : 3. concentration : 10^{-3} mol l^{-1}.

Exciting compound **2** with λ^{EX} = 388 nm, fluorescence maxima were observed at λ^{EM} = 448 and 560 nm, indicating that the shoulders at 520 and 560 nm (see Fig.3) are two more fluorescence maxima. Excitation of **1** with λ^{EX} = 450 nm led to fluorescence at 530 nm, similar to compound **1**, but with less intensity.

Using only 2-propanol as solvent, fluorescence maxima were found at 440 and 520 nm (excited with λ^{EX} = 372 nm).

Exciting compound **3** (solvent : 2-propanol/water 2 : 3) with light of λ^{EX} = 375 nm (similar to compound **1**) led to fluorescence emission at 430 nm (maximum) with a shoulder at 510 nm (see Fig.4). Exciting compound **3** with λ^{EX} = 450 nm gave light emission with its maximum at 540 nm. Using only 2-propanol as solvent led to a decrease of fluorescence intensity :

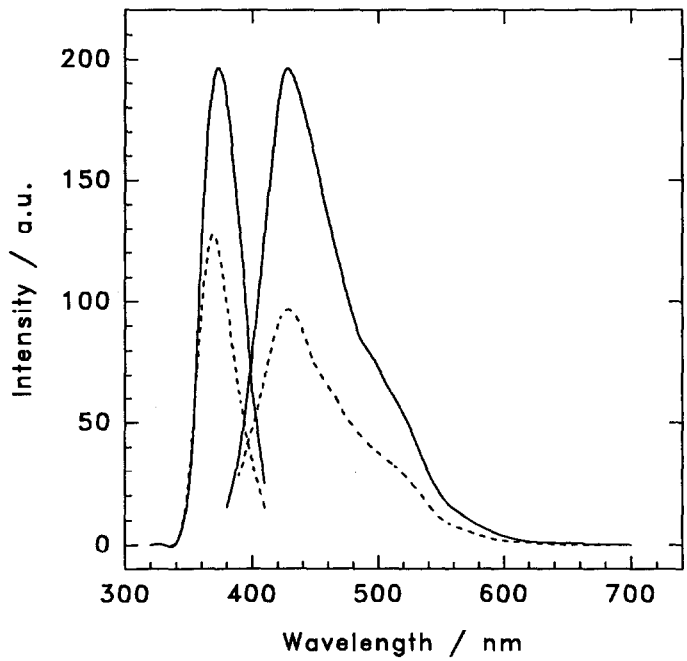


Fig.4 Fluorescence and excitation spectra of compound **3**; concentration : 10^{-3} mol l^{-1}; solvent : 2-propanol/water 2 : 3 (————) and 2-propanol (— — —).

Investigations of the fluorescence properties of compound **1** in water/2-propanol 3 : 2 resulted in one intensive fluorescence maximum at 503 nm with its excitation maximum at 453 nm (see Fig.5 and Table III).

Studying the fluorescence behavior of compound **1** in 1-propanol or acetonitrile (see Table II), fluorescence maxima with less intensities could be observed at about 530 nm.

TABLE III. Fluorescence data of compounds **1 - 4.**

sensitizer compound	concentration [mol/l]	λ^{EX} [nm]	λ^{EM} [nm]	I [a.u.]
1[2]	10^{-3}	453	503	375
1[4]	10^{-3}	393	530	3
1[5]	10^{-3}	400	531	12
2[2]	10^{-3}	375	439	323
		375	525	155
		389	560	250
		450	533	63
2[3]	10^{-3}	372	520	57
		391	510	70
		391	445	56
3[1]	10^{-3}	375	429	196
		450	540	36
3[3]	10^{-3}	370	428	128
4[1]	10^{-3}	373	465	68
		450	525	43
4[3]	10^{-3}	363	460	18

[1] 2-propanol / water 2:3, [2] 2-propanol / water 3:2, [3] 2-propanol, [4] propanol, [5] acetonitrile.

The fluorescence properties of compound **4** showed a similar behavior according to the other pyrrolizinone derivatives. Exciting compound **4** with λ^{EX} = 373 nm, the maximum of fluorescence intensity was found at 465 nm, where a higher intensity could be observed in solutions of mixtures of 2-propanol/water (2:3). Excitation with λ^{EX} = 450 nm gave another fluorescence maximum at 525 nm (also seen as shoulder in Fig.6).

The smaller fluorescence intensities found for compound **1 - 4** in alcoholic solutions was attributed to quenching effects of the organic solvent.

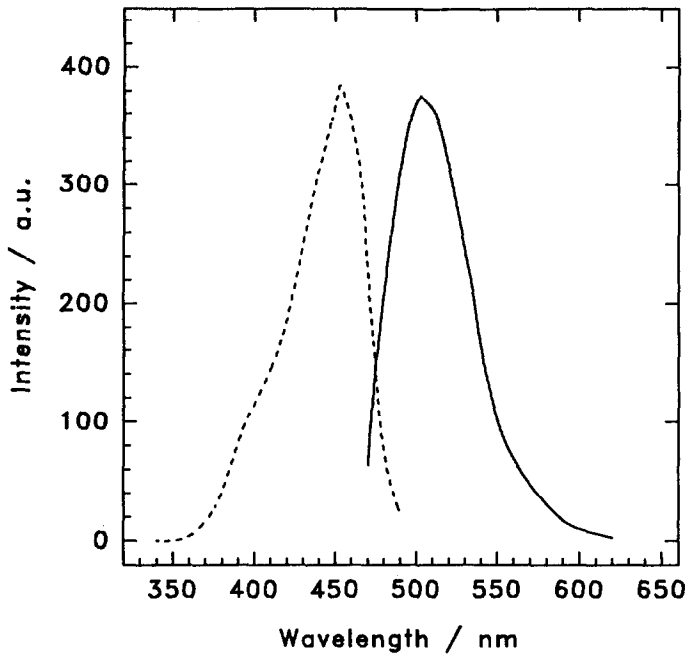


Fig.5 Fluorescence (————, λ^{EX} = 453 nm) and excitation (– – – –, λ^{EM} = 503 nm) spectra of compound **1** in 2-propanol / water = 2 : 3, concentration : 10^{-3} mol l^{-1}.

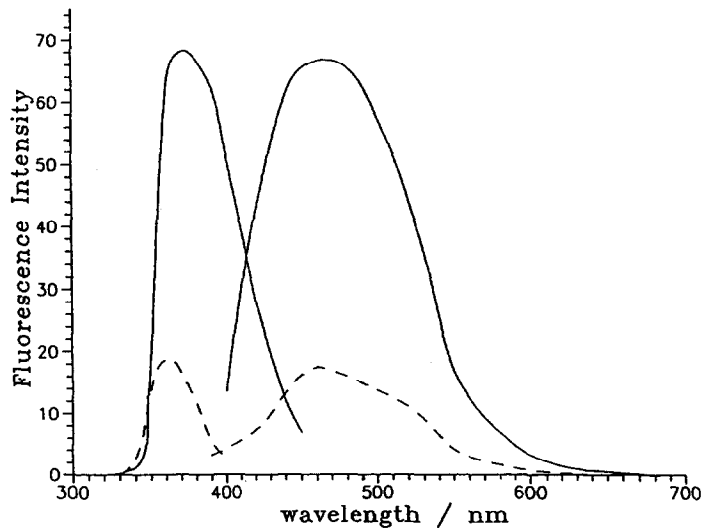


Fig.6 Fluorescence (λ^{EX} = 373 nm) and excitation spectra (λ^{EM} = 465 nm) of compound **4**; concentration : 10^{-3} mol l^{-1}; solvent : ——— : 2-propanol / water = 2 : 3, - - - - : 2-propanol.

3. *Irradiation Experiments.* Irradiation of solutions containing a sensitizer (i.e. compound **1** - **4**), 2-propanol, and methyl viologen with light $\lambda > 280$ nm, led to the formation of reduced viologen radicals. The reaction rates were found in the order of **1** > **2** > **3** > **4**. Reduction of methylviologen (in the presence of 2-propanol and compound **1** -**4**) was not possible, when the solutions were irradiated with light $\lambda > 400$ nm.

CONCLUSIONS

As absorptions and fluorescence measurements have shown, compounds **1** - **4** possess sufficient high absorbances in the visible light region, and gave fluorescence maxima, when excited both with near UV light and visible light. Compound **1** had the highest fluorescence intensity in the visible and gave the best rate for the MV^{2+} - reduction, too. However, the attempt to use compounds **1** - **4** as sensitizer for the visible region for the reduction of methyl viologen failed.

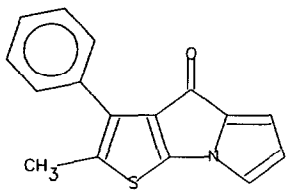
EXPERIMENTAL DETAILS

Melting points (uncorrected) : Kofler microscope; the nuclear magnetic resonance (^{1}H-n.m.r.) spectra were recorded with a Perkin Elmer R 12 A, 60 MHz (all data in ppm, standard : TMS; s = singlet, m = multiplet, sh = signal heap);
Microelementar analysis (MEA) were carried out by the Institute of Physical Chemistry, University of Vienna. For all measurements twice distilled water was used. All experiments were performed at room temperature.

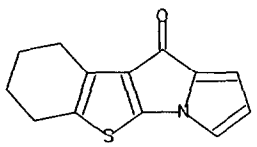
Experimental details of spectroscopy, fluorescence, and irradiation experiments were described elsewhere[26].

Syntheses

The new thieno[2,3-b]pyrrolizinone derivatives **1** - **4** were prepared[17-25] according to scheme 3 :



1



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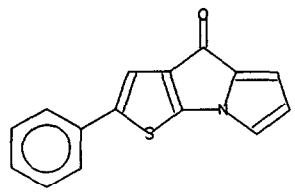

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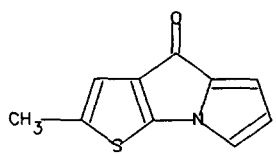
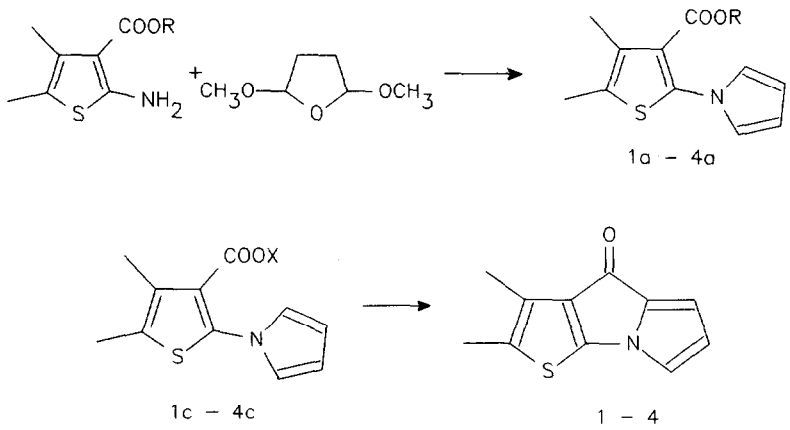


4



Scheme 3 Syntheses of compounds **1 - 4**

Ethyl-2-(1-pyrrolyl)-4-phenyl-5-methylthiophen-3-carboxylate (1a)

58g (0.422 mol) 2,5-dimethoxy tetrahydrofuran were added to a solution of 57g (0.218 mol) ethyl-2-amino-4-phenyl-5-methylthiophen-3-carboxylate[24], dissolved in 500 ml acetic acid. After refluxing at 100 - 110°C for 8 min, the solution was poured on ice and was made alkaline with KOH. This solution was extracted with ether. The organic part was washed with water and dried over Na_2SO_4. The raw product was distilled at 154°C / 10^{-3} Torr. Yield (80%) : 53.3 g, m.p. : 45-47°C. - MEA : calc. C, 69.43%; H, 5.50%; N, 4.49% found C, 68.90%; H, 5.69%; N, 4.29%. - ^{1}H-n.m.r. : 7.30 ppm (m,5H), 6.90 ppm (m,2H), 6.26 ppm (m,2H), 3.93 ppm (q,2H), 2.26 ppm (s,3H), 0.87 ppm (t,3H).

2-(1-Pyrrolyl)-4-phenyl-5-methylthiophen-3-carboxylic acid (1b)

50 g (0.161 mol) ethyl-2-(1-pyrrolyl)-4-phenyl-5-methylthiophen-3-carboxylate (**1a**) and 44 g KOH were heated under reflux for 45 min in 380 ml ethanol. The reaction mixture was poured in water and acidified with HCl. The aqueous solution was extracted with ether, the ethereal solution was dried with Na_2SO_4. The crude product

was recrystallized from cyclohexane/ether (= 1:1). Yield (90%) : 41 g, m.p.: 153-154°C. - MEA : calc. C, 67.82%; H, 4.62%; N, 4.94%; found C, 67.83%; H, 4.74%; N, 4.91%. - ^{1}H-n.m.r. : 7.35 ppm (m,5H), 6.91 ppm (m,2H), 6.30 ppm (m,2H), 2.25 ppm (s,3H), 10.77 ppm (s,broad,1H).

N,N-Dimethyl-2-(1-pyrrolyl)-4-phenyl-5-methylthiophen-3-carboxamide (1c)

16.7 (80 mmol) g PCl_5 were added in small portions to a solution of 300 ml abs. benzene containing 20 g (80 mmol) 2-(1-pyrrolyl)-4-phenyl-5-methyl-thiophene-3-carboxylic acid **(1b)** and stirred for 30 min. This solution was added dropwise to 100 ml cooled N,N-dimethylamine (60% in water) - the temperature should not exceed 30°C - and stirred for 1 hour. The reaction mixture was poured in water and was extracted with ether, the organic layer was dried with Na_2SO_4. The crude product was recrystallized from cyclohexane. Yield (90%) : 19.7 g, m.p.: 115-116°C. - MEA : calc. C, 69.60%; H, 5.80%; N, 9.02; found C, 69.60%; H, 5.93%; N, 8.95%. - ^{1}H-n.m.r. : 7.30 ppm (m,5H), 6.91 ppm (m,2H), 6.21 ppm (m,2H), 2.74 ppm (s,3H), 2.55 ppm (s,3H), 2.34 ppm (s,3H).

8H-6-Methyl-7-phenylthieno[2,3-b]pyrrolizin-8-one (1)

11 g (35.5 mmol) N,N-Dimethyl-2-(1-pyrrolyl)-4-phenyl-5-methylthiophen-3-carboxamide **(1c)** was dissolved in 60 ml $POCl_3$ and stirred for 19 h at 90°C. Then the reaction mixture was poured on ice, was made alkaline with KOH, and was extracted with $CHCl_3$. The organic layer was washed with water and dried with Na_2SO_4. The raw product was chromatographed on a column (length 29 cm, dia. 1.7 cm, filled with silica gel 60, 0.040-0.063 mm, 230-400 mesh ASTM, eluent : benzene). Recrystallization from 2-propanol yielded (42.5%) 4 g colorless crystals; m.p.: 140-141°C. - MEA : calc. C, 72.42%; H, 4.18%; N, 5.28%; found C, 72.13%; H, 4.28%; N, 5.23%. - ^{1}H-n.m.r. : 7.39 ppm (m,5H), 6.69 ppm (m,1H), 6.53 ppm (m,1H), 6.03 ppm (m,1H), 2.30 ppm (s,3H).

Ethyl-2-(1-pyrrolyl)-4,5,6,7-tetrahydrobenzo[b]thiophen-3-carboxylate (2a)

26 g (0.197 mol) 2,5-Dimethoxytetrahydrofuran was added to a solution of 23.3g (0.104 mol) ethyl ester of 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylic acid[24], dissolved in 100 ml acetic acid. After refluxing at 100 - 110°C for 5 min, the dark brown solution was poured on ice, made alkaline with KOH and extracted with ether. The organic part was washed with water and dried with Na_2SO_4. For purification the raw product was distilled at 130°C / 10^{-3} Torr. Yield (85%) : 24.4 g. - MEA : calc. C, 65.43%; H, 6.22%; N, 5.09%; found C, 65.92%; H, 6.40%; N, 5.23%. - ^{1}H-n.m.r. : 6.75 ppm (m,2H), 6.20 ppm (m,2H), 4.08 ppm (q,2H), 2,70 ppm (sh, 4H), 1.80 ppm (sh, 4H), 1.10 ppm (t,3H).

2-(1-Pyrrolyl)-4,5,6,7-tetrahydrobenzo[b]thiophen-3-carboxylic acid (2b)

35 g KOH and 33 g (0.12 mol) ethyl-2-(1-pyrrolyl)-4,5,6,7-tetrahydrobenzo[b]thiophen-3-carboxylate **(2a)** were dissolved in 170 ml ethanol at 50°C. The precipitate was dissolved in water, acidified with conc. Hcl and extracted with ether. The organic part was washed with water and dried with Na_2SO_4. After removing the ether, the precipitate was recrystallized from cyclohexane. Yield (94%) : 27.9 g, m.p.: 172°C. - MEA : calc. C, 63.13%; H, 5.30%; N, 5.66%; found C, 63.15%; H, 5.34%; N, 5.63%. - ^{1}H-n.m.r. : 11.00 ppm (s,broad, 1H), 6.81 ppm (m,2H), 6.21 ppm (m,2H), 2,70 ppm (sh, 4H), 1.80 ppm (sh, 4H).

N,N-Dimethyl-2-(1-pyrrolyl)-4,5,6,7-tetrahydrobenzo(b)thiophen-3-carboxamide (2c)

19.2 g (92 mmol) PCl_5 was added in small portions to a solution of 100 ml abs. benzene containing 21.4 g (87 mmol) 2-(1-pyrrolyl)-4,5,6,7-tetrahydrobenzo[b]thiophen-3-carboxylic acid **(2b)** and stirred for 30 min. This

solution was added dropwise to 100 ml cooled N,N-dimethylamine (60% in water) below 30°C and stirred for 1 h. The reaction mixture was poured in water and was extracted with ether, the organic part was washed with water and dried with Na_2SO_4. After removing the solvent, the raw product was purified by distillation ($p = 10^{-3}$ torr, 130-180°C). Yield (94%) : 22.4 g, m.p.: 99-100°C. - MEA : calc. C, 65.66%; H, 6.61%; N, 10.21%; found C, 65.72%; H, 6.74%; N, 10.18%. - ^{1}H-n.m.r. : 6.88 ppm (m,2H), 6.28 ppm (m,2H), 3.00 ppm (s,3H), 2.90 - 2.32 ppm (s + sh,7H), 1.86 ppm (sh,4H).

10H-6,7,8,9-Tetrahydro[1]benzothieno[2,3-b]pyrrolizin-10-one (2)

6.6 g (24 mmol) N,N-Dimethyl-2-(1-pyrrolyl)-4,5,6,7-tetrahydrobenzo[b]thiophen-3-carboxamide (**2c**) were dissolved in 100 ml abs. 1,2-dichloroethane. To this solution 21.6 g (142 mmol) $POCl_3$ were added and the solution was stirred for 12.5 h at 85°C. The reaction mixture was poured on ice, made alkaline with KOH and extracted with $CHCl_3$. The organic part was washed with water and dried over Na_2SO_4. After removing the solvent, the residue was dissolved in ether and treated with activated carbon. The raw product was recrystallized from 2-propanol. Yield (80%) : 4.4 g orange crystals, m.p.: 164-165°C. - MEA : calc. C, 68.10%; H, 4.83%; N, 6.12%; found C, 68.19%; H, 4.86%; N, 6.08%. - ^{1}H-n.m.r. : 6.72 ppm (m,1H), 6.58 ppm (m,1H), 6.10 ppm (m,1H), 2.69 ppm (sh,4H), 1.90 ppm (sh,4H).

Ethyl-2-(1-pyrrolyl)-5-phenylthiophen-3-carboxylate (3a)

8.9 g (67 mmol) 2,5-Dimethoxy tetrahydrofuran were added to a solution of 15.4 g (0.218 mol) ethyl-2-amino-4-phenyl-5-methylthiophen-3-carboxylate[24], dissolved in 100 ml acetic acid. After refluxing at 100 - 110°C for 8 min, the solution was poured on ice and made alkaline with KOH and extracted with ether. The organic part was washed with water and dried over Na_2SO_4. The raw product was distilled (150-200°C, $p = 10^{-3}$ Torr). Yield (95%) : 17.6 g, m.p.: 68-70°C. - MEA : calc. C, 68.66%; H, 5.08%; N, 4.71%; found C, 68.45%; H, 5.24%; N, 4.71%. - ^{1}H-n.m.r. : 7.70 - 7.20 ppm (sh,6H), 6.97 ppm (m,2H), 6.30 ppm (m,2H), 4.25 ppm (q,2H), 1.25 ppm (t,3H).

N-Methyl-N-phenyl-2-(1-pyrrolyl)-5-phenylthiophen-3-carboxylamide (3b)

3.4 g (23.9 mmol) Methyl iodide was added slowly to 0.6 g magnesium in 15 ml abs. ether (Grignard reaction). 2.5 g (24 mmol) N-Methylaniline, dissolved in 10 ml abs. ether, was added to the Grignard solution. The mixture reacted violently. After the end of the reaction, 3.5 g (12 mmol) ethyl-2-(1-pyrrolyl)-5-phenylthiophen-3-carboxylate (**3a**), dissolved in 60 ml abs. ether were added during 10 min, and stirred for further 20 min. Then 30 ml water were added slowly to the reaction mixture. The reaction mixture was acidified with 2n Hcl (to dissolve the basic magnesium salts). The aqueous solution was extracted with ether. After evaporation the raw product was purified by distillation ($p = 5.10^{-4}$ Torr, 110-160°C). Yield (90%) : 3.8 g, m.p. 96-97°C. - MEA : calc. C, 73.72%; H, 5.06%; N, 7.82%; found C, 72.89%; H, 5.14%; N, 7.71%. - ^{1}H-n.m.r. : 7.60 - 7.00 ppm (sh,9H), 6.80 - 6.50 ppm (sh,4H), 6.28 ppm (m,2H), 3.32 ppm (s,3H).

8H-6-Phenylthieno[2,3-b]pyrrolizin-8-one (3)

2.1 g (5.9 mmol) N-Methyl-N-phenyl-2-(1-pyrrolyl)-5-phenylthiophen-3-carboxamide (**3b**) were dissolved in 20 ml abs. 1,2-dichloroethane. To this solution 5 g (32.57 mmol) $POCl_3$ were added and stirred for 35 h at 85°C. The reaction mixture was poured on ice, made alkaline with KOH and extracted with $CHCl_3$. The organic part was washed with water and dried over Na_2SO_4. After removing the solvent, the precipitate was extracted with ether. The ethanol solution was treated with activated carbon. The raw product was purified by sublimation in vacuo ($p= 10^{-3}$ Torr, 150-200°C). Yield (75%) : 1.1 g orange crystals, m.p.: 152-154°C. - MEA : calc. C, 71.69%; H, 3.61%; N, 5.57%; found C, 71.53%; H, 3.74%; N, 5.55%. - ^{1}H-n.m.r. : 7.60 -

7.20 ppm (m,5H), 7.12 ppm (s,1H), 6.81 ppm (m,1H), 6.66 ppm (m,1H), 6.15 ppm (m,1H).

Ethyl-2-(1-pyrrolyl)-5-methylthiophen-3-carboxylate (4a)
51 g (0.386 mol) 2,5-Dimethoxytetrahydrofuran were added to a solution of 48 g (0.259 mol) ethyl-2-amino-5-methylthiophen-3-carboxylate [24], dissolved in 250 ml acetic acid. After refluxing at 100 - 110°C for 8 min, the dark brown solution was poured on ice and made alkaline with KOH. This solution was extracted with ether. The organic part was washed with water and dried over Na_2SO_4. For purification the raw product was distilled at 98°C / 10^{-3} Torr. Yield (87%) : 53.3 g. - MEA : calc. C, 61.25%; H, 5.57%; N, 5.95%; found C, 60.98%; H, 5.75%; N, 5.87%. - ^{1}H-n.m.r. : 6.99 ppm (1H), 6.82 ppm (m,2H), 6.21 ppm (m,2H), 4.12 ppm (q,2H), 2.35 ppm (3H), 1.13 ppm (t,3H).

2-(1-Pyrrolyl)-5-methylthiophen-3-carboxylic acid (4b)
43.3 g (0.184 mol) Ethyl-2-(1-pyrrolyl)-5-methylthiophen-3-carboxylate (**4a**), and 60.8 g KOH were refluxed for 1 h in 250 ml (50%) aqueous methanol. The reaction mixture was poured on ice, acidified with conc. HCl, and extracted with ether. The organic part was washed with water and dried over Na_2SO_4. After removing the solvent the raw product was recrystallized from 2-propanol. Yield (90%) : 34.2 g, m.p. 130-131°C; - MEA : calc. C, 57.95%; H, 4.28%; N, 6.76%; found C, 58.11%; H, 4.46%; N, 6.75%. - ^{1}H-n.m.r. : 10.62 ppm (s,broad,1H), 7.09 ppm (1H), 6.98 ppm (m,2H), 6.25 ppm (m,2H), 2.41 ppm (3H).

N-Methyl-N-phenyl-2-(1-pyrrolyl)-5-methylthiophen-3-carboxyamide (4c)
1.6 (7.6 mmol) g PCl_5 were added in small portions to a solution of 25 ml abs. benzene containing 1.5 g (80 mmol) 2-(1-pyrrolyl)-5-methylthiophen-3-carboxylic acid (**4b**) and stirred for 1 h. This solution was added dropwise, below 30°C, to 15 ml cooled benzene, containing 1.9 g (18 mmol) N-methylaniline and stirred for 5 min. The reaction mixture was poured on water. After extraction with ether, the organic solution was washed with aqueous Hcl and water and then dried over Na_2SO_4. The raw product was purified by distillation (p = 5.10^{-4} Torr, 110-160°C). Yield (98%) : 2.1 g. - MEA : calc. C, 68.89%; H, 5.44%; N, 9.45%; found C, 67.90%; H, 5.45%; N, 9.24%. - ^{1}H-n.m.r. : 7.40 ppm (s,1H), 7.20 - 7.00 ppm (m,3H), 6.75-6.40 ppm (sh,4H), 6.20 ppm (m,2H), 3.29 ppm (s,3H), 2.35 ppm (s,3H).

8H-Methylthieno[2,3-b]pyrrolizin-8-one (4)
2 g (6.5 mmol) N-Methyl-N-phenyl-2-(1-pyrrolyl)-5-methylthiophen-3-carboxamide (**4c**) was dissolved in 50 ml abs. 1,2-dichloroethane. To this solution 5 g (36.2 mmol) $POCl_3$ were added and the solution was stirred for 10 h at 85°C. The reaction mixture was poured on ice, made alkaline by KOH and extracted with $CHCl_3$. The organic layer was washed with water and dried over Na_2SO_4. After removing the solvent, the residue was extracted with ether. The organic part was treated with activated carbon. The raw product was recrystallized from 2-propanol. Yield (78%) : 1 g, orange crystals, m.p.: 118-119°C. - MEA : calc. C, 63.46%; H, 3.73%; N, 7.40%; found C, 63.19%; H, 3.83%; N, 7.42%. - ^{1}H-n.m.r. : 6.72 ppm (m,1H), 6.58 ppm (m,2H), 6.08 ppm (m,1H), 2.39 ppm (s,3H).

Acknowledgement : We would like to thank Prof. Dr. Karl Eichinger (Inst. of Organic Chemistry) and Prof. Dr. Osman El Dusouqui for stimulating discussions and the 'Fonds zur Förderung der Wissenschaftlichen Forschung' (Project number 8346-CHE) and the 'Hochschuljubiläumsstiftung der Stadt Wien' for their financial support.

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