Revue Roumaine de Chimie, **2009**, *54*(11-12), 927–934

Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)

PYRYLIUM SALTS WITH LONG ALKYL SUBSTITUENTS. 2,6-DIPALMITOYL- AND 2,6-DISTEAROYL-3,4-DIMETHYL PYRYLIUM SALTS, DERIVED PYRIDINES AND PYRIDINIUM SALTS**

Mariana Viorica BOGĂȚIAN,[a*] Anca HÎRTOPEANU,[a] Alina NICOLESCU,[a,b] Gheorghe BOGĂȚIAN,[c] Călin DELEANU,[a,b] Maria MAGANU[a] and Petru FILIP[a]

[a] "Costin D. Nenițescu" Institute of Organic Chemistry, Roumanian Academy, Spl. Independentei 202-B, P.O. Box 35-108, RO-060023 Bucharest, Roumania.
[b] "Petru Poni" Institute of Macromolecular Chemistry, Group of Biospectroscopy, Aleea Grigore Ghica 41-A, RO-700487, Iași, Roumania.
[c] S.B.S. Industrial Solutions, Biesterfeld Gruppe, 256 Basarabia Bvd., Bucharest, Roumania.

Received December 9, 2008

Two isomers, 2,4,6-tri- and 2,3,4,6-tetrasubstituted pyrylium salts having in 2,6-positions a palmitoyl or a stearoyl group were synthesized and characterized. N-methylpyridinium salts and derived pyridines were obtained by reaction of corresponding pyrylium salts with methyl amine or ammonia. The structures of these new compounds were confirmed by their elemental analysis, IR,UV-Vis, ^{1}H and ^{13}C NMR spectra.

INTRODUCTION

In the previous paper we described the synthesis and surfactant properties of N-phenylpyridinium chlorides. The relationship critical micellar concentration (CMC) *vs* number of carbon atoms of alkyl side chains for these new compounds was also reported.[1]

The diacylation of 2-methyl-2-butene and 2-methyl-1-butene which may be obtained *in situ* by dehydration of t-amylalcohol was investigated by A. T. Balaban. Using usual conditions (excess Ac_2O and equimolar ratio of t-amylalcohol: perchloric acid) a mixture of 80% tetra- and 20% tripyrylium salts was obtained.[2]

The selectivity of the diacetylation of olefins in dependence with the structure and positions of the alkyl substituents at heterocyclic ring and molar ratio $AcCl:AlCl_3$ has been studied by C. Roussel et. al.[3] Thus, for 2-chloro-2-methylpentane as olefin precursor, the more substituted pyrylium derivatives were obtained when using an equimolar ratio catalyst : acetylating agent.

Pyrylium salts and derived pyridines and pyridinium salts with different long alkyl substituents on the heterocyclic ring have been intensively studied in our laboratory for the last 20 years.[1,4-9] The greatest difficulty in obtaining these compounds is the separation of the pure organic pyrylium salts with various long alkyl substituents by chromatography.

The present study provides evidence for the similarity of the reaction of t-amyl chloride with different long n-alkyl (stearoyl or palmitoyl) chlorides to that of previously described compounds having short substituents at heterocyclic ring.[4]

Our main interest, however, was to synthesize new six-membered aromatic heterocycles, pyrylium perchlorates or pentachlorostannates with long alkyl substituents using the diacylation of

** This is contribution no. 16 in the series "Pyrylium Salts with Long Alkyl Substituents". For some previous papers in this series see ref. [1,4-9]

* To whom correspondence should be addressed mbogat1@cco.ro

t-amyl chloride with different acyl chlorides under a variety of conditions. The selectivity of the diacylation reaction and the synthesis of the corresponding pyridines and N-methylpyridinium perchlorates are also presented.

RESULTS AND DISCUSSION

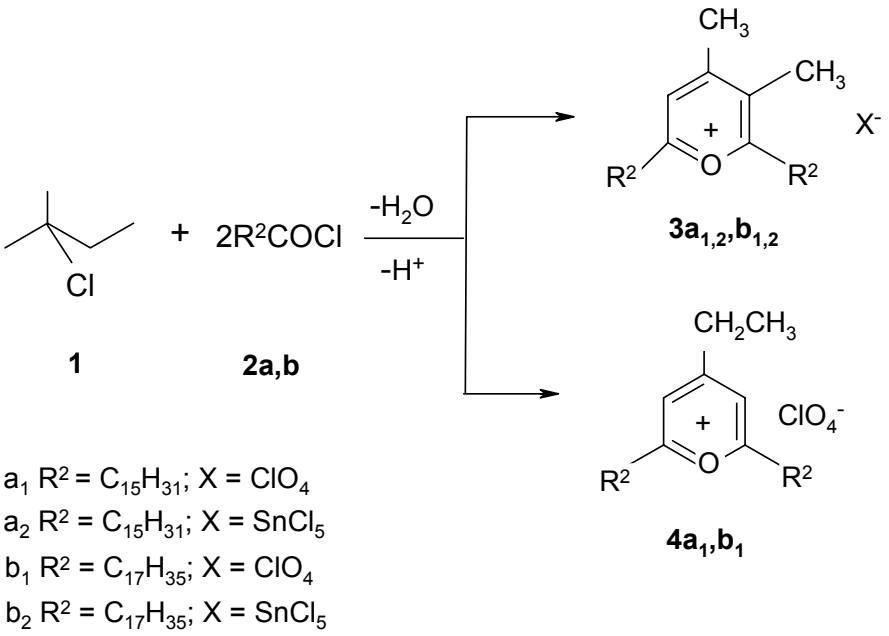
Materials and Methods

The diacylation of t-amyl derivatives with different molar ratios of catalyst : acylating agent is used as an easy route to the synthesis of tri- or tetra- substituted pyrylium salts.

We have previously examined the diacylation of 2-chloro-2-methylbutane with lauroyl chloride using $SnCl_4$ as catalyst in 1:2:2 molar ratio. In this conditions only the 2,3,4,6-tetrasubstituted pyrylium salt (perchlorate or pentachlorostannate) was obtained.[4]

In this paper, we present the acylation of t-amyl chlorides with stearoyl or palmitoyl chlorides. We have examined the dependence of the selectivity on the molar ratio RCOCl : $SnCl_4$.

Our first attempt to synthesi ze the 2,4,6-tri- or 2,3,4,6-tetrasubstituted pyrylium salts **3a$_{1,2}$,b$_{1,2}$** and **4a$_1$,b$_1$** is summarized in **Scheme 1**.



Scheme 1 – The synthesis of new pyrylium salts.

It is well known that the effect of weaker Lewis acids and the ratio of RCOCl : Lewis acid play an important role on the acylation selectivity.[10-11]

Both these long acyl chlorides **2a,b** react with t-amyl chloride **1** in different way compared to undecyl chloride. In these cases 2,6-dialkyl-4-ethylpyrylium salts in low yields (under 30%) were also obtained. (see **Table 1**, experiments 1-4 *vs* 5).

This fact is also supported by (i) the GC/MS analysis after conversion of the mixture pyrylium salts to the corresponding pyridines and (ii) the obtaining of both pure pyrylium salts (see experimental part).

For the synthesis of pyrylium pentachlorostannates we have modified the previously[4] described procedure. Based on these results, we prepared and increased the yields of new pentachlorostannates **3a$_2$**, **3b$_2$** using different molar ratios RCOCl : $SnCl_4$ (see **Table 1**).

The reaction of pyrylium pentachlorostannates with perchloric acid followed by column chromatography separation, as previously was reported,[4, 5b-c,6,8,9a] afforded the corresponding pyrylium perchlorates in pure state with high yields (22-25%).

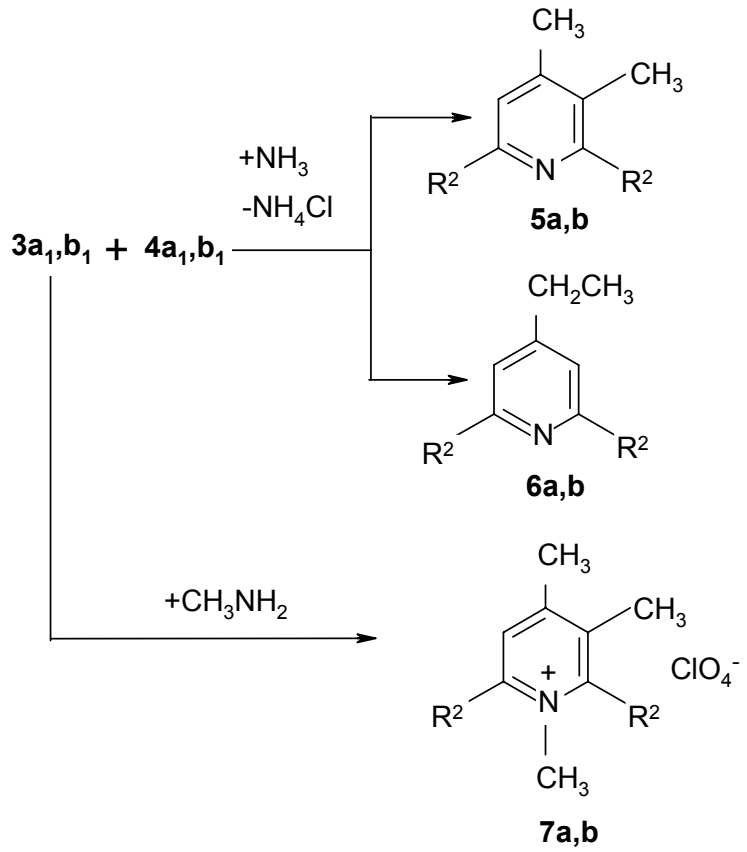
For the synthesis of the pyridines **5a,b**, **6a,b** and the N-methylpyridinium perchlorate **7a,b** (**scheme 2**) we have followed the same classical protocol by reaction between salts with ammonia or methylamine. The conditions giving the best yields as well as the purification procedures are given in the experimental part.

Table 1

Experimental data

Exp.	Molar Ratio RCOCl : $SnCl_4$	Pyrylium salts[a]		Yield,[b] %					
		$3a_1$:$4a_1$	**$3b_1$:$4b_1$**	**$3a_1$**	**$3b_1$**	**$4a_1$**	**$4b_1$**	**$3a_2$**	**$3b_2$**
1	1 : 1	95 :5	-	19.7	-	3.1	-	-	-
2	1 : 1	-	92 : 8	-	20.1	-	2.9	-	-
3	1 : 1.3	78 : 22	-	22.8	-	8.9	-	10.1	-
4	1 : 1.3	-	72 : 28	-	24.3	-	9.5	-	11.5
5	1 : 1	only **$3a_1$**	-	18.1	-	-	-	5.2	-

[a] By GC / MS, after conversion in corresponding pyridines;
[b] After column chromathography or TLC separation;
[c] For $R^2 = C_{11}H_{23}$ (see [4]).



Scheme 2 – Conversion of pyrylium salts **$3a_1$,b_1** into pyridines **5a,b** – **6a,b** and into N-methyl-pyridinium perchlorate **7a,b.**

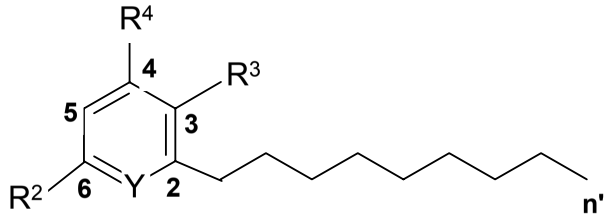
The purity for all new compounds was confirmed by ^{1}H, ^{13}C-NMR, IR , UV-VIS, GC/MS spectra and elemental analysis (see experimental part).

The ^{1}H and ^{13}C-NMR chemical shifts of **3-7** were in agreement with the previously reported NMR data. The assignments in the one dimensional ^{1}H- and ^{13}C-NMR spectra were confirmed from additional H-H COSY, H-C HMQC and H-C HMBC spectra. Practically all individual signals could be resolved in the ^{13}C-NMR spectra, but as expected for the chemical shifts of the proton in the long chains some overlapping occurs in the ^{1}H-NMR spectra (see Experimental Part).[1,4-9]

Table 2 and **Table 3** present the ^{1}H and ^{13}C-NMR chemical shifts respectivelly for these new compounds.

Tabel 2

Selected signal assignments for ^{1}H-NMR spectra (400.13 MHz) of **3a$_1$,b$_1$,4a$_1$,b$_1$,5a,b,6a,b** and **7a,b**



Y = O^+, N, N^+-CH_3

Comp. H	**O^+**				**N**				**N^+CH_3**	
	3a$_1$	**3b$_1$**	**4a$_1$**	**4b$_1$**	**5a**	**5b**	**6a**	**6b**	**7a**	**7b**
5-H	7.72	7.72	7.73	7.76	6.81	6.81	6.79	6.79	7.36	7.37
4-CH_3	2.67	2.67	-	-	2.25	2.25	-	-	2.49	2.50
3-CH_3	2.40	2.41	-	-	2.19	2.18	-	-	2.37	2.39
4-CH_2	-	-	3.03	3.04	-	-	2.32	2.33	-	-
2_2'-CH_2	3.14	3.14	3.15	3.16	2.81	2.81	2.80	2.80	3.08	3.08
2_6'-CH_2	3.08	3.09	-	-	2.71	2.70	-	-	3.01	3.02
3'-CH_2	1,83	1.82	1.78	1.19	1.67	1.67	1.64	1.65	1.73	1.74
4'-CH_2	1.40	1.41	1.38	1.38	-	-	2.32	2.33	-	-
5'-15'CH_2/ 5'-17'CH_2	1.17-1.26	1.17-1.26	1.17-1.26	1.17-1.26	1.17-1.25	1.17-1.26	1.17-1.28	1.17-1.28	1.17-1.26	1.17-1.26
n'- CH_3	0.88	0.88	0.87	0.87	0.88	0.88	0.88	0.88	0.88	0.88
n''- CH_3	-	-	1.14	1.14	-	-	1.10	1.10	-	-
N- CH_3	-	-	-	-	-	-	-	-	4.17	4.18

Table 3

Selected signal assignments for ^{13}C-NMR (100.61 MHz) of **3a$_1$,b$_1$,4a$_1$,b$_1$,5a,b,6a,b** and **7a,b**.

Comp. C	**O$^+$**				**N**				**N$^+$CH$_3$**	
	3a$_1$	**3b$_1$**	**4a$_1$**	**4b$_1$**	**5a**	**5b**	**6a**	**6b**	**7a**	**7b**
C-2	177.83	177.74	179.39	179.28	157.92	158.02	160.77	160.84	155.47	155.42
C-6	178.09	177.98	-	-	158.94	159.01	-	-	156.73	156.62
C-4	172.74	172.69	171.99	171.92	148.50	148.47	148.73	148.77	156.24	156.20
C-5	131.54	131.48	-	-	137.09	137.14	-	-	133.98	133.95
C-3	123.32	123.27	126.02	126.15	122.08	122.04	121.75	121.78	126.83	126.79
4-CH$_3$	23.56	23.57	-	-	20.26	20.29	-	-	21.51	21.50
4-CH$_2$	-	-	24,78	24.77	-	-	23.14	23.20	-	-
3-CH$_3$	14.08	14.09	-	-	14.13	14,17	-	-	15.51	15.54
2$_2$'-CH$_2$	33.25	33.18	34.19	34.20	35.37	35.38	34.04	34.09	34.08	34.15
2$_6$-CH$_2$	34.70	34.54	-	-	37.09	36.99	-	-	34.27	34.22
3'-CH$_2$	27.00	26.96	27.03	27.04	29.13	29.11	27.19	27.22	29.72	29.69
(n'-2)-CH$_2$	31.87	31.88	31.94	31.93	31.95	31.95	31.91	31.91	31.91	31.87
(n'-1)-CH$_2$	22.70	22.64	22.69	22.65	22.71	22.78	22,70	22.71	22.65	22.63
n'-CH$_3$	14.00	14.00	14.05	14.05	14.01	14.02	14.02	14.02	14.07	14.07
n''-CH$_3$	-	-	14.17	14.18	-	-	14.14	14.14	-	-
N-CH$_3$	-	-	-	-	-	-	-	-	39.75	39.68

Based on assignments of the reported GC/MS[6] for various pyridines with long alkyl substituents having either a short alkyl group,[8e] one alkyl[9a] in the α-position or isoprenoid C_{11} in the γ-position[9b] or two alkyl C_{11}[8e] in the α-position the fragmentation pattern under electron impact of the new compounds follows similar trends.

Isomeric pyridines **5a** – **6a** and **5b** – **6b** have the parent peak in the EI mass spectrum at m/z= 527 and respectively, 583.

For both 3,4-dimethyl substituted pyridines **5a,b** having a methyl group in the β-position the base peak appeared in the EI mass spectrum at m/z=135 and corresponds to the substituted benzylic type cation ($C_9H_{13}N^+$) after two McLafferty fragmentations. These results were in agreement with our previously reported data.[4]

The isomeric symmetrical pyridines **6a,b** which have one ethyl group in the γ-position present a different EI mass spectrum. In these cases, the base peak appeared in the EI mass spectrum at m/z=332 respectively, m/z=360 and corresponds to the substituted benzylic type cation $C_{23}H_{42}N^+$ or $C_{24}H_{46}N^+$ after one McLafferty fragmentation. In these cases the major peaks appeared at m/z= 148 (94.61% for **6a** and 89.61% for **6b**) and respectively, 135 (93.06% for **6a** and 81.76% for **6b**). For comparison, the 2,6-diundecyl-4-methyl pyridine had the parent peak at m/z= 261 ($C_{18}H_{31}N^+$) and the major peak (abundance 90%) at m/z=121 ($C_8H_{11}N^+$).[8e]

EXPERIMENTAL PART

The NMR spectra have been recorded on a BRUKER AVANCE 400 DRX instrument, equipped with a 5 mm inverse detection multinuclear probehead and field gradients on the z axis, operating at 400.13 MHz for ^{1}H and at 100.61 MHz for ^{13}C nuclei. The COSY45, HMQC and HMBC spectra have been recorded with standard Bruker parameters in the versions employing pulsed field gradients. All spectra have been recorded in deuterated chloroform, and the chemical shifts have been reported as δ values referenced to TMS as an internal standard. Infrared spectra were run on a BRUKER VERTEX 70 instrument equipped with a Golden Gate diamond ATR. The UV-VIS spectra were recorded with a GBC type 918 instrument in 1 cm cuvettes. Mass spectra were recorded using a Trio–1000 Fissons spectrometer connected to a Carlo Erba HRGC 5300 gas chromatograph. Emission spectrum were recorded on a ICP-AES instrument. Melting points were measured in open capillary tubes (for the low melting compounds) or on a hot-plate melting points apparatus (equipped with a polarizer to check for nematic properties).

Synthesis of pyrylium salts. General procedure.
2,6-Dipalmitoyl- 3a$_2$ and 2,6-distearoyl-3,4-dimethyl-pyrylium pentachlorostannate 3b$_2$. 2,6-Dipalmitoyl- 3a$_1$ and 2,6-distearoyl-3,4-dimethyl-pyrylium perchlorate 3b$_1$. 2,6-Dipalmitoyl- 4a$_1$ and 2,6-distearoyl-4-ethyl-pyrylium perchlorate 4b$_1$.

In a four-necked flask equipped with mechanical stirrer, imersed thermometer, reflux condenser, dropping funnel and exit protected by a $CaCl_2$ tube, $SnCl_4$ (57.4 g, 0.22 moles for experiment 1,2 and 74.5 g, 0.286 moles for experiment 3,4), was added under external cooling (ice and water bath) to palmitoyl chloride (60.48 g, 0.22 moles, experiment 1,3) or stearoyl chloride (66.65 g, 0.22 moles, experiment 2,4). The t-amyl chloride (11.72 g, 0.11moles) was added dropwise so to maintain the temperature between 22 and 25˚C.

The stirring was continued at room temperature for 48 hours. The evolution of hydrogen chloride ceased after additional stirring for 5 hours at 35 - 40˚C.

The reaction mixture was decomposed and separated by the method developed in our laboratory. The generality of this method was confirmed by the application to these new compounds. For related observations see.[4-9]

So, the reaction mixture was decomposed by pouring it over 80g crushed ice, 8 mL concentrated aqueous hydrochloric acid and 100 mL diethyl ether. The organic layer was separated and washed with 500 mL mixture distilled water : hydrochloric acid=2:1. The combined aqueous layers were colourless and clear.

The organic layer was dried and concentrated, then filtered through a sintered glass affording a reddish oil (25 - 30 g), which was deposited on silica gel Merck (70 – 230 mesh; ratio silica/oil = 2/1) and was separated on silica gel column (200g silica/1000 mL, solvent petroleum ether). The intermediates and the by-products of the acylation reaction were eluted in the forerun, as previously described.[4-9]

Pyrylium pentachlorostannate **3a$_2$** (experiment 3) and **3b$_2$** (experiment 4) was lastly eluted with a mixture of ethyl acetate : methanol = 1 : 2. From this fraction, after extraction three times with 50 mL methylene chloride, drying (over $MgSO_4$) and concentration, the pyrylium pentachlorostannate cristallised as colourless crystals with m.p.= 101-103 ˚C (9.16 g, 0.011 mole), in 10.1% yield for **3a$_2$** and respectively, m.p.= 105-107 ˚C (11.15 g, 0.013 mole) in 11.5% yield for **3b$_2$**.

Elemental analysis:

3a$_2$ **$C_{37}H_{69}SnCl_5O$** Calcd: C 53.80% H 8.36% Cl 21.51% Sn 14.38%;
Found C 53.90% H 8.30% Cl 21.50%; found by emission spectrum Sn 14.40%

3b$_2$ **$C_{41}H_{77}SnCl_5O$** Calcd: C 55.83% H 8.74% Cl 20.14% Sn 13.47%;
Found C 55.90% H 8.72% Cl 20.03%; found by emission spectrum Sn 13.40%
.

IR, ν cm $^{-1}$: 1025.44, 1480.33, 1550.24, 1630.01, 2850.15, 2920.09 (**3a$_2$**).

UV (EtOH), λ_{max} (nm): 217.4; 270.3; 373 sh (**3a$_2$**).

^{1}H-NMR ($CDCl_3$): 0.88 (t, 6H, J=6.9 Hz, 16'-CH_3), 1.26 (m, 44H, 5'-15'-CH_2), 1.35 (m, 4H, 4-CH_2), 1.78 (cv, 4H, 3'-CH_2), 2.43 (s, 3H, 3-CH_3), 2.75 (s, 3H, 4-CH_3), 3.19 (t, 2H, J=7.9 Hz, 2_6'-CH_2), 3.23 (t, 2H, J=8.0 Hz, 2_2'-CH_2), 7.86 (s, 1H, 5-H) for **3a$_2$**.

The ^{1}H-NMR, IR, UV spectra of the **3b$_2$** were in full agreement with the data for **3b$_2$** .

For preparing the pyrylium perchlorates **3a$_1$-4a$_1$** and **3b$_1$-4b$_1$** (experiment 1-4), 70% perchloric acid was added to the organic layer obtained from the aqueous work-up of the diacylation mixture. All the subsequent steps for purification were similar to those for both mixtures **3a$_1$-4a$_1$** and **3b$_1$-4b$_1$**.

The last fraction after eluting with a mixture ethyl acetate: hexane: methanol = 90:10:5 by column chromathography contains a mixture **3a$_1$-4a$_1$** (experiment 1, 3) or **3b$_1$-4b$_1$** (experiment 2, 4).

Pyrylium perchlorates **3a$_1$/3b$_1$** or **4a$_1$/4b$_1$** were obtained in pure state after a second separation by thin layer chromatogra-

phy (silica gel Merck, type 60G, solvent ethyl acetate : methanol=1:1).

So, the pyrylium perchlorates **3a$_1$** and **3b$_1$** (R_f = 0.2), after concentration and refrigeration for one hour, crystallized spontaneously with m.p.= 62-63˚C (**3a$_1$**) or 63-67˚C (**3b$_1$**). The yields in **3a$_1$** and **3b$_1$** were 22.8 % (experiment 3, 15.76 g, 25.07 mmoles) and 24.3% (experiment 4, 18.3 g, 26.74 mmoles) respectivelly.

Pyrylium perchlorates **4a$_1$** and **4b$_1$** (R_f = 0.8), were obtained after solvent evaporation, as waxy oils which crystallized on cooling. The crystals were collected on a sintered glass filter and washed twice with diethyl ether with m.p.= 30-32 ˚C (**4a$_1$**) or 33-65˚C (**4b$_1$**). The yields in **4a$_1$** and **4b$_1$** were 8.9 % (experiment 3) and 9.5% (experiment 4) respectivelly.

Elemental analysis for **3a$_1$ - 3b$_1$**:

3a$_1$ $C_{37}H_{69}ClO_5$ Calcd: C 70.64% ; H 10.98% ; Cl 5.65;
Found: C 70.65; H 10.99: Cl 5.64.

3b$_1$ $C_{41}H_{77}ClO_5$ Calcd: C 71.88% ; H 11.25% ; Cl 5.18;
Found: C 71.86%; H 11.30%; Cl 5.19%.

IR ν, cm^{-1}: 622.99, 722.11, 1083.20, 1376.11, 1466.07, 1528.32, 1628.33, 2849.99, 2918.44 (**3a$_1$**); 622.99, 722.11, 1083.60, 1320.90, 1376.11, 1469.10, 1528.48, 2852.16, 2918.44; 2990.01 (**4a$_1$**);

UV (C_2H_5OH), λ_{nm} (max): 217.4; 246.9; 370 sh (**3a$_1$**) and 207.5; 235.3; 381sh (**4a$_1$**).

The IR and UV spectra of the **3b$_1$** and **4b$_1$** were in full agreement with the data for **3a$_1$ / 4a$_1$**.

2,6-Dipalmitoyl- and 2,6-distearoyl-3,4-dimethylpyridines 5a,b -6a,b

Pyrylium perchlorates **3a$_1$**,**b$_1$** or **4a$_1$**,**b$_1$** (1.2 mmoles) were treated with aqueous ammonia (20%). The pyridines ***5a,b-6a,b*** were extracted in diethyl ether; drying over potassium hydroxide pellets and concentration in vacuum, yielded yellow oils.

The yields were 75% (**5a**), 72% (**5b**), 76% (**6a**) and 75% (**6b**) respectively.

$C_{37}H_{69}N$ (5a) Calcd: N 2.66%;
Found: N 2.64%.

$C_{41}H_{77}N$ (5b) Calcd: N 2.40%;
Found: N 2.43%.

GC/MS (m/z):

527 (M^+), 485, 471, 457, 443, 429, 415, 401, 387, 373, 359, 345, 332 (65.32%), 302, 288, 274, 260, 246, 232, 204, 190, 162, 148 (83.76%), 135 (100%), 121, 79, 57, 43 (**5a**)

527 (M^+), 485, 471, 457, 443, 429, 415, 401, 387, 373, 345, 332 (100%), 303, 288, 274, 260, 246, 232, 204, 190, 162, 148(94.61%), 135 (93.06%), 121, 79, 57, 43 (**6a**)

583 (M^+), 555, 541, 529, 499, 485, 471, 457, 443, 429, 415, 401, 387, 373, 360 (61.60 %), 345, 331, 316, 302, 288, 274, 260, 246, 204, 190, 148 (79.66 %), 135 (100 %), 121, 57, 43 (**5b**)

583 (M^+), 555, 541, 527, 499, 485, 471, 457, 443, 429, 415, 401, 387, 373, 360 (100 %), 345, 331, 316, 302, 288, 274, 260, 246, 204, 190, 148 (89.61 %), 135 (81.76 %), 121, 57, 43 (**6b**).

IR ν, cm^{-1}: 721.26, 1370.45, 1462.25, 1562.81, 1596.69, 1718.49, 2326.99, 2851.24, 2930.11 (**5a**); 720.69, 1465.90, 1562.81, 1603.84, 1719.39, 2362.02, 2850.58, 2918.11(**5b**).

UV (C_2H_5OH), λ_{nm} (max): 219.2; 268.5 (**5a**); 220.1; 270.1(**5b**).

The IR and UV spectra of the **6a** and **6b** were in full agreement with the data for **5a / 5b**.

N-methyl-2,6-dipalmitoyl- 7a and N-methyl-2,6- distearoyl - 3,4- dimethyl pyridinium perchlorate 7b

Pyridinium salts **7a** and **7b** were prepared according to the following general procedure: to the solution of pyrylium salt **3a$_1$** or **3b$_1$** in ethanol an excess of amine (solution 40% wt. in ethanol was added (molar ratio 1:5); a deep-red colour developed instantly. The mixture was heated at a gentle reflux of the solvent, for one hour when the colour of the solution turned to cognac. The pyridinium salts crystallized spontaneously; after refrigeration for one hour, the crystals were collected on a sintered glass filter and washed twice with diethyl ether; recrystallization from i-propanol gave colourless crystals with m.p.= 92-93 ˚C for **7a** and for 85-86 ˚C **7b**.

$C_{28}H_{72}NClO_4$ (7a) Calcd: N 2.18%;
Found: N 2.19%.

$C_{42}H_{80}NClO_4$ (7b) Calcd: N 2.01%;
Found: N 1.99%.

IR ν, cm^{-1}: 622.06, 720.19, 1078.97, 1264.95, 1378.64, 1415.34, 1486.00, 1566.41, 1627.25, 2849.20, 2917.25, 2917.25, 3065.22 (**7a**); 622.08, 718.81, 1082.19, 1268.98, 1378.58, 1417.41, 1468.47, 1572.66, 1628.93, 2849.64, 2916.42, 2917.25, 3069.75 (**7b**)

UV (C_2H_5OH), λ_{nm} (max): 212.2; 275.5 (**7a**); 214.0; 274.9 (**7b**).

Acknowledgements: The authors are grateful to Mrs. Marieta Plăveți for recording the elemental microanalyses. Thanks are expressed to Dr. Cornelia Uncuța and Dr. Teodor Silviu Balaban for permanent interest and helpful discussions. The financial support from the Ministry of Education and Research through the PNCDI2 CNMP Project CELLPHARM Grant no. 41-047-3 / 2007 and FARMACRO Grant no. 61-028-2 / 2007 are warmly acknowledged.

REFERENCES

1. M. V. Bogățian, A. Hîrtopeanu, A. Nicolescu, F. Chiraleu, M. Maganu, M. Vînătoru, D. Simion and C. Deleanu, *Rev. Roum. Chim.*, **2008**, *53*, 431.
2. a) A. T. Balaban and A. Bota, Organic Preparation and Procedures Int., **1982**, *14*, 31; b) A. T. Balaban and C. D. Nenitescu, J. Chem. Soc., **1961**, 3553.
3. M Arnaud, C. Roussel and J. Metzger, Tetrahedron Lett., **1979**, *20*, 1795.
4. M. V. Bogățian, V. Campeanu, S. Serban, G. Mihai and T. S. Balaban, *Rev. Roum. Chim.*, **2001**, *46*, 115.
5. a)M. V. Bogățian, A. C. Corbu, C. Deleanu, M. Maganu and G. Bogățian, *Rev. Roum. Chim.*, **2007**, *52*, 181; b)M. V. Bogățian, C. Deleanu, D. Simion (Nuță), M. Maganu, A. C. Corbu, F. Chiraleu and G. Bogățian, *Rev. Roum. Chim.*, **2006**, *51*, 273; c)M. V. Bogățian, G. Bogățian, S. Udrea, A. C. Corbu, F. Chiraleu, M. Maganu and C. Deleanu *Rev. Roum. Chim.*, **2006**, *51*, 735.
6. M. V. Bogățian, *Ph. D. Thesis*, Roumanian Academy, "Costin D. Nenitzescu" Institute of Organic Chemistry, 1998.
7. M. V. Bogățian, V. Campeanu, C. Deleanu, A. C. Corbu, G. Bogățian and T. S. Balaban, *ARKIVOC*, **2005**, 272-284 (http://www.arkatusa.org/ark/ journal /2005 /I10_ Balaban/1275/AB-1275B.pdf).
8. a) M. V. Bogățian, M. Vinatoru, G. Bogățian, G. Mihai and T. S. Balaban, *Rev. Roum. Chim.*, **2004**, *49*, 829; b) M. V. Bogățian, C. Deleanu, S. Udrea, F. Chiraleu, M.

Plăveti, M. G. Danilă, G. Bogățian and T. S. Balaban*, Rev. Roum.Chim.,* **2003**, *48*, 717; c)M. V. Bogățian, V. Campeanu, S. Serban, G. Mihai and T. S. Balaban*, Rev. Roum. Chim.,* **2001**, *46*, 115; d)M. V. Bogățian, G. Mihai, M. Plăveți, F. Chiraleu, M. Maganu, V. Bădescu and T. S. Balaban, *Rev. Roum.Chim.*, **1998**, *43*, 315; e)M. V. Bogățian, G. Mihai, M. Plăveți, F.Chiraleu, C. Deleanu, V. Bădescu and T. S. Balaban, *Rev Roum. Chim.*, **1996**, *41*, 979.

9. a)M. V. Bogățian, C. Deleanu, G. Mihai and T. S. Balaban, *Z. Naturforsch.*, **1992**, *47b*, 1011; b)T. S. Balaban , M. V. Bogățian, M. Plăveti, V. Bădescu and G. Mihai, *Rev Roum. Chim.,* **1991**, *36*, 229.
10. A.T. Balaban, A. Dinculescu, G. N. Dorofeenko, G. W. Fischer, A. V. Kobilik, V. V. Mezheritskii and W. Scroth, "Pyrylium Salts. Syntheses, Reactions and Physical Properties", Adv. Heterocyclic Chem., Suppl. vol. 2, A. R.. Katritzky, Ed. Academic Pess, New-York, **1984**.
11. a)A.T. Balaban and C. D. Nenitescu, Tetrahedron Lett., 1960, 2,7; b)A. Bota, A.T. Balaban and F. Chiraleu, Rev. Roum, Chim., **1976**, *21*,101.