Ring Transformations of Heterocyclic Compounds. X [1]. A Simple Method for the Conversion of Methyl Substituted Pyridinium Salts into 2,4,6-Triarylphenyl Derivatives: The First (Thio)Pyrylium Ring Transformations with Heterocyclic Anhydrobases as Carbon Nucleophiles

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The synthesis of 2,4,6-triarylphenylpyridinium perchlorates **3** from methyl substituted derivatives **2** by a 2,6-[C_5+C] ring transformation of 2,4,6-triaryl(thio)pyrylium salts **1/4** in the presence of triethylamine/acetic acid in ethanol is reported. Spectroscopic data of the pyridinium perchlorates **3** and their formation *via* anhydrobases of the salts **2** are discussed.

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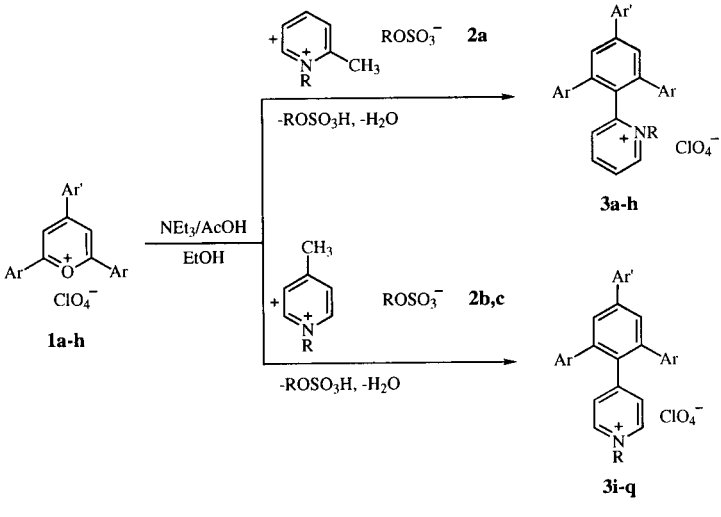
Ring transformation reactions of pyrylium salts represent valuable methods for the preparation of a wide variety of carbocyclic and heterocyclic compounds [2]. Although the related reactions of thiopyrylium salts [3] usually lead to products which can be synthesized more easily from the pyrylium analogues some examples of preparative value are known [4,5]. In the first step of the transformations a nucleophile is added to the (thio)-pyrylium cation and then by ring opening/ring closure a new ring is constructed. As carbon nucleophile compounds with an activated methyl(ene) group, metal organic reagents, ylids or enamines have been used [2,3]. The first transformations with enamines were described by Märkl *et al.*, who found that 2,4,6-triarylpyrylium salts react with enamines derived from cyclic ketones to give benzophenones and/or benzocycloalkenes [6,7]. Later it was shown that enamines are the key intermediates in transformations of pyrylium salts with methyl(ene) ketones [8]. In case of thiopyrylium salts it was found that the addition of acetone leading to 2-acetonyl-2*H*-thiopyrans proceeds *via* acetonenamines [9] but ring transformations have not been published.

It has been known for a long time that cationic heterocycles with a suitable positioned methyl(ene) group can be deprotonated to give anhydrobases [10] which possess an integrated enamine structure. Since transformations of (thio)pyrylium salts with these types of compounds have never been reported we became interested in exploring such reactions. In this paper we wish to present our first results obtained with pyridinium salts [11].

When the 2,4,6-triarylpyrylium perchlorates **1a-h** and the 1,2-dimethylpyridinium methosulfate (**2a**) were refluxed in ethanol in the presence of triethylamine and acetic acid (molar ratio **1a-h**:**2a**:NEt_3:AcOH=1:1:3:2) the 2-(2,4,6-triarylphenyl)-1-methylpyridinium perchlorates **3a-h** were formed by pyrylium ring transformation. Under the same conditions from the salts **1a-h** and the 4-methyl substituted pyridinium salts **2b,c** the 4-(2,4,6-triarylphenyl)pyridinium perchlorates **3i-q** were obtained. Contrary to the 2- and 4-methylpyridinium derivatives **2a-c** the 3-methyl isomers gave no ring transformation products. If the perchlorates instead of the methylpyridinium methosulfates or ethosulfates **2** were used the reaction was slower since these salts are less soluble in



1	2	Ar	Ar'	R	3
a	**a**	Ph	Ph	Me	**a**
b	**a**	Ph	4-Me-C_6H_4	Me	**b**
c	**a**	Ph	4-MeO-C_6H_4	Me	**c**
d	**a**	Ph	4-Cl-C_6H_4	Me	**d**
e	**a**	Ph	4-Br-C_6H_4	Me	**e**
f	**a**	4-Me-C_6H_4	Ph	Me	**f**
g	**a**	4-Cl-C_6H_4	Ph	Me	**g**
h	**a**	4-Br-C_6H_4	Ph	Me	**h**
a	**b**	Ph	Ph	Me	**i**
b	**b**	Ph	4-Me-C_6H_4	Me	**j**
c	**b**	Ph	4-MeO-C_6H_4	Me	**k**
d	**b**	Ph	4-Cl-C_6H_4	Me	**l**
e	**b**	Ph	4-Br-C_6H_4	Me	**m**
f	**b**	4-Me-C_6H_4	Ph	Me	**n**
g	**b**	4-Cl-C_6H_4	Ph	Me	**o**
h	**b**	4-Br-C_6H_4	Ph	Me	**p**
a	**c**	Ph	Ph	Et	**q**

ethanol and in some cases the transformation products obtained were contaminated with unreacted starting materials. Furthermore, treatment of the 2,4,6-triarylpyrylium perchlorates **1** with the iodides of **2** resulted in the isolation of an iodide/perchlorate mixture of products. Hence, it is necessary to use such educts that the reaction mixture contains only one anion which is able to precipitate the 2,4,6-triarylphenylpyridinium cation.

The trimethylpyridinium methosulfates **2d,e** possess two reactive C-bonded methyl groups and besides the transformation with one equivalent of the pyrylium salt **1** a twofold transformation should be possible. When the 1,2,6-trimethylpyridinium methosulfate (**2d**) was treated with 2,4,6-triphenylpyrylium perchlorate (**1a**) in a 1:1-molar ratio the expected product **3r** was obtained. In case of the 1,2,4-trimethylpyridinium methosulfate (**2e**) the less reactive 2-methyl group [12] remained unchanged and the 1,2-dimethyl-4-(2,4,6-triphenylphenyl)pyridinium perchlorate (**3s**) was formed. Surprisingly, when the salts **2d,e** were treated with two equivalents of **1a** or the isolated 2,4,6-triphenylphenylpyridinium perchlorates **3r,s** with one equivalent of **1a** in a separate step no bistransformation products could be isolated.

The ring transformations described for the pyrylium salts can be extended to the related thiopyrylium salts. As shown for the 2,4,6-triphenylthiopyrylium perchlorate (**4**) by treatment with the methylpyridinium methosulfates **2a,b** in the presence of triethylamine/acetic acid in boiling ethanol the 2,4,6-triphenylphenylpyridinium perchlorates **3a,i** were formed which are identical with the compounds obtained from the pyrylium perchlorate **1a** and **2a,b**. Since the products were formed in lower yields and

Table 1

Physical and Analytical Data for the 2,4,6-Triarylphenylpyridinium Perchlorates **3a-s**

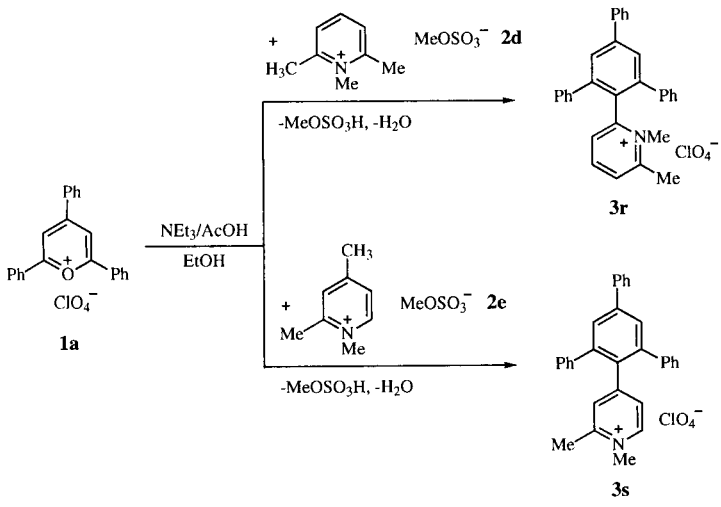
No.	-pyridinium perchlorate	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N
3a	1-methyl-2-(2,4,6-triphenylphenyl)-	64	248-250	$C_{30}H_{24}ClNO_4$ (498.0)	72.36 72.20	4.86 4.92	2.81 2.85
3b	1-methyl-2-[4-(4-methylphenyl)-2,6-diphenylphenyl]-	51	255-256	$C_{31}H_{26}ClNO_4$ (512.0)	72.72 72.68	5.12 5.08	2.74 2.80
3c	2-[4-(4-methoxyphenyl)-2,6-diphenylphenyl]-1-methyl-	48	145-146	$C_{31}H_{26}ClNO_5$ (528.0)	70.52 70.40	4.96 5.00	2.65 2.60
3d	2-[4-(4-chlorophenyl)-2,6-diphenylphenyl]-1-methyl-	48	237-238	$C_{30}H_{23}Cl_2NO_4$ (532.4)	67.68 67.60	4.35 4.38	2.63 2.65
3e	2-[4-(4-bromophenyl)-2,6-diphenylphenyl]-1-methyl-	70	279-281	$C_{30}H_{23}BrClNO_4$ (576.9)	62.46 62.40	4.02 4.02	2.43 2.45
3f	1-methyl-2-[2,6-bis(4-methylphenyl)-4-phenylphenyl]-	46	245-246	$C_{32}H_{28}ClNO_4$ (526.0)	73.07 73.11	5.37 5.31	2.66 2.62
3g	2-[2,6-bis(4-chlorophenyl)-4-phenylphenyl]-1-methyl-	66	301-302	$C_{30}H_{22}Cl_3NO_4$ (566.9)	63.57 63.50	3.91 3.90	2.47 2.46
3h	2-[2,6-bis(4-bromophenyl)-4-phenylphenyl]-1-methyl-	62	295-296	$C_{30}H_{22}Br_2ClNO_4$ (655.8)	54.95 54.94	3.38 3.39	2.14 2.06
3i	1-methyl-4-(2,4,6-triphenylphenyl)-	85	301-302	$C_{30}H_{24}ClNO_4$ (498.0)	72.36 72.20	4.86 4.81	2.81 2.80
3j	1-methyl-4-[4-(4-methylphenyl)-2,6-diphenylphenyl]-	84	265-266	$C_{31}H_{26}ClNO_4$ (512.0)	72.72 72.70	5.12 5.10	2.74 2.80
3k	4-[4-(4-methoxyphenyl)-2,6-diphenylphenyl]-1-methyl-	81	261-263	$C_{31}H_{26}ClNO_5$ (528.0)	70.52 70.70	4.96 4.99	2.65 2.68
3l	4-[4-(4-chlorophenyl)-2,6-diphenylphenyl]-1-methyl-	72	283-285	$C_{30}H_{23}Cl_2NO_4$ (532.4)	67.68 67.73	4.35 4.38	2.63 2.70
3m	4-[4-(4-bromophenyl)-2,6-diphenylphenyl]-1-methyl-	78	280-282	$C_{30}H_{23}BrClNO_4$ (576.9)	62.46 62.50	4.02 4.10	2.43 2.45
3n	1-methyl-4-[2,6-bis(4-methylphenyl)-4-phenylphenyl]-	49	225-226	$C_{32}H_{28}ClNO_4$ (526.0)	73.07 73.10	5.37 5.40	2.66 2.68
3o	4-[2,6-bis(4-chlorophenyl)-4-phenylphenyl]-1-methyl-	73	295-297	$C_{30}H_{22}Cl_3NO_4$ (566.9)	63.57 63.60	3.91 3.95	2.47 2.50
3p	4-[2,6-bis(4-bromophenyl)-4-phenylphenyl]-1-methyl-	71	306-307	$C_{30}H_{22}Br_2ClNO_4$ (655.8)	54.95 54.97	3.38 3.40	2.14 2.16
3q	1-ethyl-4-(2,4,6-triphenylphenyl)-	76	318-319	$C_{31}H_{26}ClNO_4$ (512.0)	72.72 72.80	5.12 5.10	2.74 2.79
3r	1,2-dimethyl-6-(2,4,6-triphenylphenyl)-	41	264-265	$C_{31}H_{26}ClNO_4$ (512.0)	72.72 72.81	5.12 5.20	2.74 2.76
3s	1,2-dimethyl-4-(2,4,6-triphenylphenyl)-	24	345-346	$C_{31}H_{26}ClNO_4$ (512.0)	72.72 72.80	5.12 5.15	2.74 2.76

Table 2

Spectral Data for the 2,4,6-Triarylphenylpyridinium Perchlorates **3a-s**

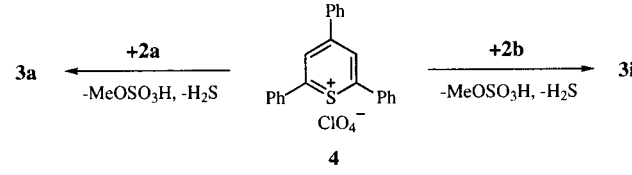
Compound	IR (KBr) (cm^{-1}) ClO_4	UV (CH_3CN) λ_{max} (nm) (log ε)	^{1}H-NMR (DMSO-d_6) [a] δ (ppm)
3a [b]	1095	247 (4.64), 310 (3.99)	3.80 (s, 3H, NCH_3), 7.16-8.34 (m, 20H, arom H), 8.75 (d, J = 5.9 Hz, 1H, 6-H)
3b	1097	251 (4.60), 314 (4.01)	2.31 (s, 3H, CH_3), 3.79 (s, 3H, NCH_3), 7.15-8.32 (m, 19H, arom H), 8.74 (d, J = 5.6 Hz, 1H, 6-H)
3c	1095	255 (4.47), 289 sh (4.26), 327 sh (3.98)	3.76 (s, 3H, OCH_3), 3.80 (s, 3H, NCH_3), 7.01-8.33 (m, 19H, arom H), 8.74 (d, J = 5.9 Hz, 1H, 6-H)
3d	1098	251 (4.61), 309 (4.02)	3.80 (s, 3H, NCH_3), 7.16-8.35 (m, 19H, arom H), 8.75 (d, J = 5.8 Hz, 1H, 6-H)
3e	1092	252 (4.65), 309 sh (4.09)	3.80 (s, 3H, NCH_3), 7.16-8.34 (m, 19H, arom H), 8.76 (d, J = 5.8 Hz, 1H, 6-H)
3f	1095	252 (4.67), 315 (3.95)	2.21 (s, 6H, CH_3), 3.79 (s, 3H, NCH_3), 7.06-8.35 (m, 18H, arom H), 8.76 (d, J = 5.9 Hz, 1H, 6-H)
3g	1097	253 (4.69), 309 (3.90)	3.81 (s, 3H, NCH_3), 7.20-8.40 (m, 18H, arom H), 8.78 (d, J = 5.8 Hz, 1H, 6-H)
3h	1093	253 (4.73), 311 sh (4.03)	3.82 (s, 3H, NCH_3), 7.13-8.40 (m, 18H, arom H), 8.79 (d, J = 5.5 Hz, 1H, 6-H)
3i [b]	1093	240 (4.66), 325 (4.11)	4.14 (s, 3H, NCH_3), 7.14-7.71 (m, 19H, arom H), 8.58 (d, J = 6.6 Hz, 2H, 2-H/6-H)
3j	1097	240 (4.65), 331 (4.15)	2.27 (s, 3H, CH_3), 4.14 (s, 3H, NCH_3), 7.13-7.69 (m, 18H, arom H), 8.57 (d, J = 6.7 Hz, 2H, 2-H/6-H)
3k	1096	239 (4.61), 340 (4.13)	3.74 (s, 3H, OCH_3), 4.15 (s, 3H, NCH_3), 6.97-7.66 (m, 18H, arom H), 8.58 (d, J = 6.9 Hz, 2H, 2-H/6-H)
3l	1097	245 (4.63), 324 (4.15)	4.16 (s, 3H, NCH_3), 7.13-7.86 (m, 18H, arom H), 8.60 (d, J = 6.9 Hz, 2H, 2-H/6-H)
3m	1091	245 (4.63), 324 (4.18)	4.15 (s, 3H, NCH_3), 7.12-7.80 (m, 18H, arom H), 8.59 (d, J = 6.7 Hz, 2H, 2-H/6-H)
3n	1096	248 (4.68), 330 (4.07)	2.22 (s, 6H, CH_3), 4.16 (s, 3H, NCH_3), 7.03-7.79 (m, 17H, arom H), 8.59 (d, J = 6.4 Hz, 2H, 2-H/6-H)
3o	1095	246 (4.69), 323 (4.11)	4.18 (s, 3H, NCH_3), 7.15-7.83 (m, 18H, arom H), 8.64 (d, J = 6.7 Hz, 2H, 2-H/6-H)
3p	1097	248 (4.74), 324 (4.14)	4.17 (s, 3H, NCH_3), 7.08-7.83 (m, 18H, arom H), 8.64 (d, J = 6.6 Hz, 2H, 2-H/6-H)
3q	1097	241 (4.65), 327 (4.12)	1.33 (t, J = 7.3 Hz, 3H, CH_3), 4.42 (q, J = 7.3 Hz, 2H, NCH_2), 7.12-7.73 (m, 19H, arom H), 8.70 (d, J = 6.9 Hz, 2H, 2-H/6-H)
3r	1097	247 (4.59), 314 (4.31)	2.56 (s, 3H, CH_3), 3.70 (s, 3H, NCH_3), 7.16-8.17 (m, 20H, arom H)
3s	1097	244 (4.65), 318 (4.14)	2.44 (s, 3H, CH_3), 4.02 (s, 3H, NCH_3), 7.13-7.83 (m, 19H, arom H), 8.54 (d, J = 6.6 Hz, 1H, 6-H)

[a] 2-H/6-H denotes the protons in 2-/6-position and arom H the other protons of pyridinium ring and the 2,4,6-triarylphenyl substituent. [b] Mass spectra (FAB): m/z **3a** 398 [$C_{30}H_{24}N^+$], **3i** 398 [$C_{30}H_{24}N^+$].

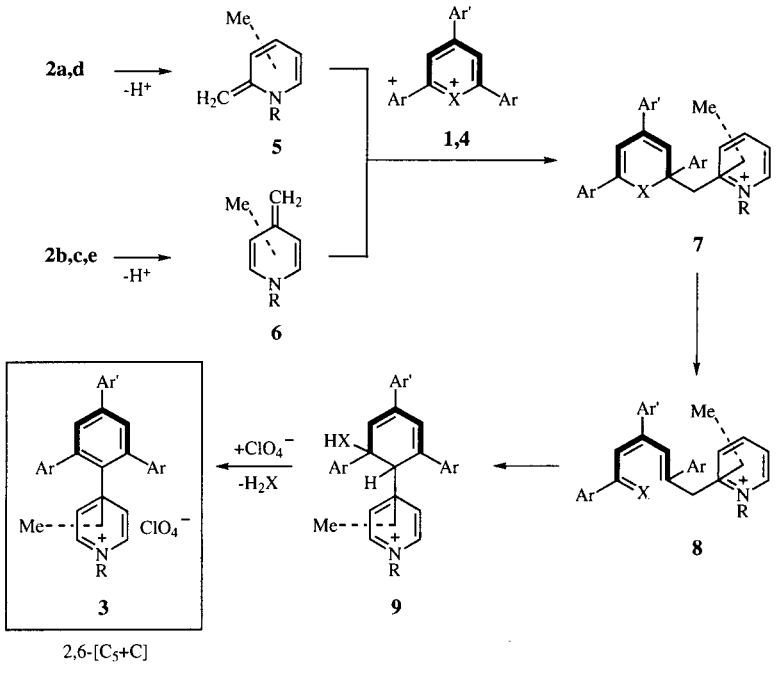


thiopyrylium salts of type **4** are usually prepared by heteroatom exchange of pyrylium salts according to the Wizinger procedure [3,13] the synthesis of 2,4,6-triarylphenylpyridinium derivatives is more convenient starting from the pyrylium salts **1**. The ring transformations **1** + **2** → **3** and **4** + **2** → **3** offer a simple possibility for the conversion of methylpyridinium salts into 2,4,6-triarylphenyl derivatives which represent pyridinium salts with a new substitution pattern.

The results of the elemental analyses and the spectroscopic data (*cf.* Tables 1 and 2) are in agreement with the



structure of the 2,4,6-triarylphenylpyridinium perchlorates **3a-s**. A characteristic feature of the ^{1}H nmr spectra is the expected doublet of the protons in α-position of the pyridinium ring [14] at 8.74-8.79 ppm (**3a-h**) and 8.57-8.64 ppm (**3i-g**), respectively, which is significantly downfield shifted in comparison with the signals of the protons bonded to the aryl substituents. The *N*-methyl group in **3a-h** causes a singlet at 3.79-3.82 ppm whereas the same *N*-methyl group in **3i-p** resonates at 4.14-4.18 ppm. Since nOe experiments clearly indicate that in the transformation product of the pyrylium perchlorate **1a** with 1,2,4-



trimethylpyridinium methosulfate (**2e**) the *N*-methyl substituent is in close proximity to a methyl group it can be concluded that **3s** was formed and not the other possible isomer (1,4-dimethyl-2-(2,4,6-triphenylphenyl)pyridinium perchlorate) where these two groups are far away from each other. In the uv spectra a strong absorption at 240-255 nm and another band of lower intensity at 309-340 nm are observed. The results of the elemental analyses and the typical ClO_4-absorption [15] at 1091-1098 cm^{-1} show that perchlorate salts were isolated.

For the interpretation of the reaction mechanism of the transformations observed it can be assumed that in the first step the methylpyridinium salts **2a-e** are deprotonated by triethylamine to the corresponding anhydrobases **5** and **6**, respectively [11]. The 3-methyl substituted isomers gave no ring transformation since here the formation of anhydrobases is impossible. Then **5** and **6** are added to the preferred position 2 of the 2,4,6-triaryl(thio)pyrylium cations **1/4** to give 2*H*-(thio)pyran intermediates **7** [2,3,16]. By ring opening to **8**, recyclization to cyclohexadienes **9** and elimination of H_2X (X = O,S) the 2,4,6-triarylphenylpyridinium salts **3** are formed. In the course of the reaction a benzene ring is built up from five carbon atoms of the (thio)pyrylium cation and the C-atom of the carbon bonded methyl group of the pyridinium salt by connection of the former positions 2 and 6 of the heterocycles **1/4** by one carbon atom. Hence, the reaction can be characterized as a 2,6-[C_5+C] transformation [17]. Furthermore, these reactions represent the first (thio)pyrylium ring transformations with heterocyclic anhydrobases as carbon nucleophiles.

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus and are corrected. The ^1H nmr spectra were recorded on a Varian Gemini 200 spectrometer (199.975 MHz, DMSO-d_6, 25°, HMDSO as the internal standard), ir spectra were obtained on a Zeiss M 80 spectrophotometer (in potassium bromide) and uv spectra on a Zeiss M 40 instrument (acetonitrile, 25°). Mass spectra were determined on a Finnigan MAT 701A spectrometer (FAB, 8 keV, argon, matrix: nitrobenzyl alcohol). The pyrylium salts **1a** [18], **1b** [19], **1c** [20], **1d** [21], **1e** [22], **1f-h** [23] and the thiopyrylium salt **4** [13] were prepared according to literature procedures; the methylpyridinium salts **2a-e** were synthesized applying standard methods for the alkylation of pyridines with dialkyl sulfates [24].

Preparation of 2,4,6-Triarylphenyl Substituted Pyridinium Perchlorates **3** from 2,4,6-Triarylpyrylium Salts **1** and Methylpyridinium Salts **2**. General Procedure (*cf.* Tables 1 and 2).

To absolute ethanol (40 ml) 5 mmoles pyrylium perchlorate **1**, 5 mmoles pyridinium salt **2**, triethylamine (1.51 g, 15 mmoles) and acetic acid (0.60 g, 10 mmoles) were added. The reaction mixture was then heated under reflux for 2 hours. The triarylphenylpyridinium perchlorates **3** formed crystallized in some cases from the hot reaction mixture; otherwise their crystallization was initiated by cooling. They were filtered off by suction, washed with ethanol and diethyl ether and recrystallized from ethanol/acetone (**3a-f**, **3i-o**, **3r**) or ethanol/acetone/acetonitrile (**3g,h**, **3p,q**, **3s**).

When the pyridinium methosulfates **2d,e** were treated with two equivalents of 2,4,6-triphenylpyrylium perchlorate (**1a**) only the monotransformation products **3r** (31%) and **3s** (11%) were isolated.

Synthesis of the 2,4,6-Triphenylphenylpyridinium Perchlorates

3a,i from 2,4,6-Triphenylthiopyrylium Perchlorate (**4**) and the Methylpyridinium Methosulfates **2a,b**.

According to the general procedure for the transformation of pyrylium salts **1** 2,4,6-triphenylthiopyrylium perchlorate (**4**) (2.12 g, 5 mmoles) was reacted with the methylpyridinium methosulfates **2a,b** and triethylamine/acetic acid in ethanol. The products were isolated and purified as described there. Yields: **3a** 43%, **3i** 55%; the compounds were identical in all respects with the ones obtained from **1a** and **2a,b**.

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