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The preparation of hitherto unknown 2,4,6-triarylphenyl substituted quinolinium perchlorates **3** from methylquinolinium derivatives **2** by a 2,6-[C₅+C] ring transformation of 2,4,6-triaryl(thio)pyrylium salts **1/4** in the presence of triethylamine/acetic acid is described. Spectroscopic data of the quinolinium perchlorates **3** and their formation *via* anhydrobases of the salts **2** are discussed.

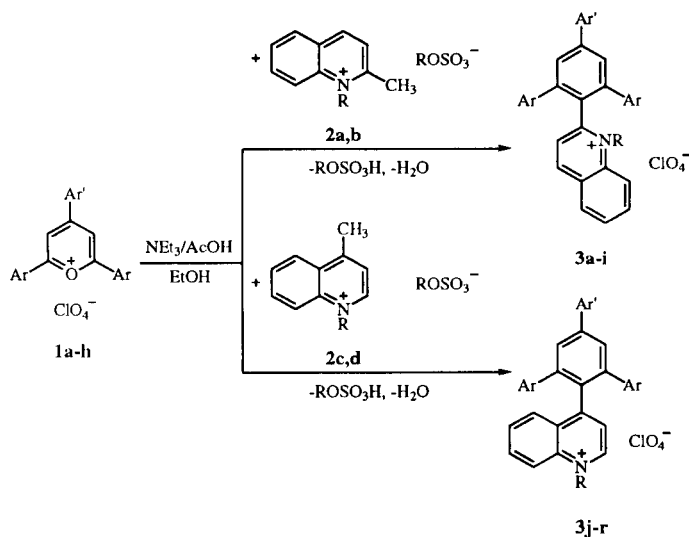
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In the preceding paper of this series [1] we described a simple method for the conversion of 2- and 4-methyl substituted pyridinium salts into 2,4,6-triarylphenyl derivatives by pyrylium [2] and thiopyrylium [3] ring transformation, respectively. As key intermediates anhydrobases of the methylpyridinium salts which act as carbon nucleophiles with an integrated enamine structure were discussed. Our continuous interest in extending these reactions to other heterocyclic systems capable of forming

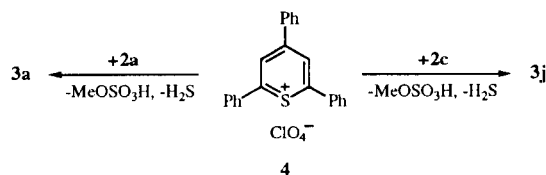
anhydrobases prompted us to study (thio)pyrylium transformations with methylquinolinium salts [4].

When the 2,4,6-triarylpyrylium perchlorates **1a-h** and the 2-methylquinolinium salts **2a,b** were heated in the presence of triethylamine/acetic acid in boiling ethanol the 2-(2,4,6-triarylphenyl)quinolinium perchlorates **3a-i** were formed (yield 57-88%) by pyrylium ring transformation. Under the same conditions the pyrylium salts **1a-h** reacted with the 4-methylquinolinium isomers **2c,d** to give the 4-(2,4,6-triarylphenyl)quinolinium perchlorates **3j-r** (yield 64-96%).

The transformations can be extended to the thiopyrylium analogues. As shown for the 2,4,6-triphenylthiopyrylium perchlorate (**4**) with the quinolinium salts **2a,c** and triethylamine/acetic acid in ethanol the same 2,4,6-triphenylphenylquinolinium perchlorates **3a,j** were obtained as from the pyrylium salt **1a** and **2a,c**. Since the yields were lower and the starting thiopyrylium salts have to be prepared by heteroatom exchange from pyrylium compounds [5] it is evident that the quinolinium salts **3** can be synthesized more effectively applying pyrylium transformations. The reaction products obtained represent quinolinium derivatives with a former unknown substitution pattern.



1	2	Ar	Ar'	R	3
a	a	Ph	Ph	Me	a
b	a	Ph	4-Me-C ₆ H ₄	Me	b
c	a	Ph	4-MeO-C ₆ H ₄	Me	c
d	a	Ph	4-Cl-C ₆ H ₄	Me	d
e	a	Ph	4-Br-C ₆ H ₄	Me	e
f	a	4-Me-C ₆ H ₄	Ph	Me	f
g	a	4-Cl-C ₆ H ₄	Ph	Me	g
h	a	4-Br-C ₆ H ₄	Ph	Me	h
a	b	Ph	Ph	Et	i
a	c	Ph	Ph	Me	j
b	c	Ph	4-Me-C ₆ H ₄	Me	k
c	c	Ph	4-MeO-C ₆ H ₄	Me	l
d	c	Ph	4-Cl-C ₆ H ₄	Me	m
e	c	Ph	4-Br-C ₆ H ₄	Me	n
f	c	4-Me-C ₆ H ₄	Ph	Me	o
g	c	4-Cl-C ₆ H ₄	Ph	Me	p
h	c	4-Br-C ₆ H ₄	Ph	Me	q
a	d	Ph	Ph	Et	r



The mechanism of the ring transformations observed can be explained in analogy to the reaction of the (thio)pyrylium perchlorates **1/4** with methylpyridinium salts [1]. Under the action of triethylamine the methylquinolinium salts **2** are deprotonated to the corresponding anhydrobases which as carbon nucleophiles of the enamine type are added to the preferred position 2 of the (thio)pyrylium ring [2,3,6]. Then *via* ring opening/ring closure

Table 1
Physical and Analytical Data for the 2,4,6-Triarylphenylquinolinium Perchlorates **3a-r**

No.	Quinolinium Perchlorate	Yield (%)	Mp [a] (°C)	Molecular Formula (Molecular Weight)	Analysis (%)		
					C	H	N
3a	1-Methyl-2-(2,4,6-triphenylphenyl)-	88	335-337	C ₃₄ H ₂₆ ClNO ₄ (548.0)	74.52 74.48	4.78 4.83	2.56 2.65
3b	1-Methyl-2-[4-(4-methylphenyl)-2,6-diphenylphenyl]-	83	338-339	C ₃₅ H ₂₈ ClNO ₄ (562.1)	74.79 74.60	5.02 5.10	2.49 2.56
3c	2-[4-(4-Methoxyphenyl)-2,6-diphenylphenyl]-1-methyl-	81	319-321	C ₃₅ H ₂₈ ClNO ₅ (578.1)	72.72 72.65	4.88 4.80	2.42 2.46
3d	2-[4-(4-Chlorophenyl)-2,6-diphenylphenyl]-1-methyl-	87	336-338	C ₃₄ H ₂₅ Cl ₂ NO ₄ (582.5)	70.11 70.11	4.33 4.28	2.40 2.46
3e	2-[4-(4-Bromophenyl)-2,6-diphenylphenyl]-1-methyl-	87	346-348	C ₃₄ H ₂₅ BrClNO ₄ (626.9)	65.14 65.10	4.02 4.10	2.23 2.30
3f	1-Methyl-2-[2,6-bis(4-methylphenyl)-4-phenylphenyl]-	69	299-300	C ₃₆ H ₃₀ ClNO ₄ (576.1)	75.06 75.10	5.25 5.18	2.43 2.40
3g	2-[2,6-Bis(4-chlorophenyl)-4-phenylphenyl]-1-methyl-	76	210-212 293-294	C ₃₄ H ₂₄ Cl ₃ NO ₄ (616.9)	66.19 66.20	3.92 3.95	2.27 2.30
3h	2-[2,6-Bis(4-bromophenyl)-4-phenylphenyl]-1-methyl-	84	275-277	C ₃₄ H ₂₄ Br ₂ ClNO ₄ (705.8)	57.86 57.94	3.43 3.50	1.98 2.00
3i	1-Ethyl-2-(2,4,6-triphenylphenyl)-	57	277-278	C ₃₅ H ₂₈ ClNO ₄ (562.1)	74.79 74.82	5.02 5.10	2.49 2.35
3j	1-Methyl-4-(2,4,6-triphenylphenyl)-	81	363-364	C ₃₄ H ₂₆ ClNO ₄ (548.0)	74.52 74.55	4.78 4.73	2.56 2.51
3k	1-Methyl-4-[4-(4-methylphenyl)-2,6-diphenylphenyl]-	74	310-312	C ₃₅ H ₂₈ ClNO ₄ (562.1)	74.79 74.71	5.02 5.10	2.49 2.55
3l	4-[4-(4-Methoxyphenyl)-2,6-diphenylphenyl]-1-methyl-	66	169-171 272-274	C ₃₅ H ₂₈ ClNO ₅ (578.1)	72.72 72.71	4.88 4.82	2.42 2.46
3m	4-[4-(4-Chlorophenyl)-2,6-diphenylphenyl]-1-methyl-	78	309-311	C ₃₄ H ₂₅ Cl ₂ NO ₄ (582.5)	70.11 70.16	4.33 4.36	2.40 2.32
3n	4-[4-(4-Bromophenyl)-2,6-diphenylphenyl]-1-methyl-	77	319-321	C ₃₄ H ₂₅ BrClNO ₄ (626.9)	65.14 65.10	4.02 4.10	2.23 2.23
3o	1-Methyl-4-[2,6-bis(4-methylphenyl)-4-phenylphenyl]-	64	346-347	C ₃₆ H ₃₀ ClNO ₄ (576.1)	75.06 75.10	5.25 5.30	2.43 2.44
3p	4-[2,6-Bis(4-chlorophenyl)-4-phenylphenyl]-1-methyl-	96	190-192 324-326	C ₃₄ H ₂₄ Cl ₃ NO ₄ (616.9)	66.19 66.24	3.92 3.93	2.27 2.28
3q	4-[2,6-Bis(4-bromophenyl)-4-phenylphenyl]-1-methyl-	84	203-204 330-332	C ₃₄ H ₂₄ Br ₂ ClNO ₄ (705.8)	57.86 57.86	3.43 3.45	1.98 1.97
3r	1-Ethyl-4-(2,4,6-triphenylphenyl)-	70	330-332	C ₃₅ H ₂₈ ClNO ₄ (562.1)	74.79 74.81	5.02 5.03	2.49 2.51

[a] Some of the quinolinium salts **3** have double melting points.

a new benzene ring is formed [7]. Since this ring is built up from five carbon atoms of the (thio)pyrylium cation **1/4** and the C-atom of the carbon bonded methyl group of the quinolinium salt by connection of the former positions 2 and 6 of **1/4** by one carbon atom the reaction can be classified as a 2,6-[C₅+C] transformation [8].

The results of the elemental analyses and the spectroscopic data (cf. Tables 1 and 2) strongly support the structure proposed for the products of the transformations **1 + 2** → **3** and **4 + 2** → **3**. In the ¹H nmr spectra the protons of the quinolinium ring in position 4 and 2 cause doublets in the expected region (**3a-i**: 8.91-8.99 ppm, **3j-r**: 9.16-9.27 ppm) [9]; these signals are significantly shifted downfield in comparison to the signals of the aryl protons. The *N*-methyl group is responsible for a singlet at 4.10-4.15 ppm (**3a-h**) and at 4.46-4.51 ppm (**3j-q**), respec-

tively. In the uv spectra a strong absorption at 241-247 nm and one to three bands of lower intensity up to 377 nm can be observed. Finally, from the results of the elemental analyses and the characteristic perchlorate-absorption [10] at 1092-1098 cm⁻¹ it can be concluded that quinolinium perchlorates were isolated.

EXPERIMENTAL

The melting points were measured on a Boëtius apparatus and are corrected. The ¹H nmr spectra were recorded on a Varian Gemini 200 spectrometer (199.975 MHz, DMSO-d₆, 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

Table 2
Spectral Data for the 2,4,6-Triarylphenylquinolinium Perchlorates **3a-r**

Compound	IR (KBr) (cm ⁻¹) ClO ₄	UV (CH ₃ CN) λ _{max} (nm) (log ε)	¹ H NMR (DMSO-d ₆) [a] δ (ppm)
3a [b]	1093	245 (4.79), 354 (4.11)	4.10 (s, 3H, NCH ₃), 7.16-8.32 (m, 22H, arom-H), 8.91 (d, J = 8.5 Hz, 1H, 4-H)
3b	1094	245 (4.87), 359 (4.21)	2.32 (s, 3H, CH ₃), 4.10 (s, 3H, NCH ₃), 7.18-8.32 (m, 21H, arom-H), 8.91 (d, J = 8.5 Hz, 1H, 4-H)
3c	1095	243 (4.80), 291 sh (4.35), 369 (4.12)	3.77 (s, 3H, OCH ₃), 4.10 (s, 3H, NCH ₃), 7.03-8.32 (m, 21H, arom-H), 8.91 (d, J = 8.8 Hz, 1H, 4-H)
3d	1095	245 (4.85), 354 (4.21)	4.11 (s, 3H, NCH ₃), 7.18-8.33 (m, 21H, arom-H), 8.92 (d, J = 8.5 Hz, 1H, 4-H)
3e	1094	245 (4.84), 354 (4.81)	4.12 (s, 3H, NCH ₃), 7.19-8.33 (m, 21H, arom-H), 8.93 (d, J = 8.8 Hz, 1H, 4-H)
3f	1097	246 (4.88), 359 (4.13)	2.11 (s, 6H, CH ₃), 4.11 (s, 3H, NCH ₃), 6.95-8.33 (m, 20H, arom-H), 8.93 (d, J = 8.5 Hz, 1H, 4-H)
3g	1097	247 (4.92), 353 (4.17)	4.14 (s, 3H, NCH ₃), 7.18-8.36 (m, 20H, arom-H), 8.98 (d, J = 8.7 Hz, 1H, 4-H)
3h	1098	246 (4.91), 351 (4.18)	4.15 (s, 3H, NCH ₃), 7.12-8.36 (m, 20H, arom-H), 8.99 (d, J = 8.4 Hz, 1H, 4-H)
3i	1095	246 (4.86), 346 (4.10)	1.03 (t, J = 7.0 Hz, 3H, CH ₃), 4.70 (q, J = 7.0 Hz, 2H, CH ₂), 7.17-8.35 (m, 22H, arom-H), 8.99 (d, J = 8.7 Hz, 1H, 4-H)
3j [b]	1093	241 (4.92), 323 (4.03), 362 sh (3.96)	4.47 (s, 3H, NCH ₃), 7.05-8.29 (m, 22H, arom-H), 9.17 (d, J = 6.4 Hz, 1H, 2-H)
3k	1092	241 (4.84), 262 sh (4.59), 323 (3.95), 365 (3.90)	2.32 (s, 3H, CH ₃), 4.46 (s, 3H, NCH ₃), 7.05-8.28 (m, 21H, arom-H), 9.16 (d, J = 6.1 Hz, 1H, 2-H)
3l	1097	241 (4.81), 263 sh (4.54), 322 (3.97), 377 (3.88)	3.77 (s, 3H, OCH ₃), 4.47 (s, 3H, NCH ₃), 7.00-8.28 (m, 21H, arom-H), 9.17 (d, J = 6.2 Hz, 1H, 2-H)
3m	1097	241 (4.84), 258 sh (4.66), 322 (3.97), 360 (3.92)	4.49 (s, 3H, NCH ₃), 7.06-8.30 (m, 21H, arom-H), 9.20 (d, J = 6.0 Hz, 1H, 2-H)
3n	1097	241 (4.83), 256 sh (4.68), 323 (3.97), 355 (3.93)	4.48 (s, 3H, NCH ₃), 7.06-8.29 (m, 21H, arom-H), 9.18 (d, J = 6.4 Hz, 1H, 2-H)
3o	1096	241 (4.83), 256 sh (4.68), 323 (3.97), 355 (3.93)	2.06 (s, 6H, CH ₃), 4.48 (s, 3H, NCH ₃), 6.82-8.31 (m, 20H, arom-H), 9.18 (d, J = 6.4 Hz, 1H, 2-H)
3p	1093	241 (4.85), 256 sh (4.69), 323 (3.95), 358 sh (3.86)	4.51 (s, 3H, NCH ₃), 7.10-8.35 (m, 20H, arom-H), 9.27 (d, J = 5.9 Hz, 1H, 2-H)
3q	1093	242 (4.87), 256 sh (4.75), 323 (3.96), 358 sh (3.88)	4.51 (s, 3H, NCH ₃), 7.00-8.35 (m, 20H, arom-H), 9.24 (d, J = 6.2 Hz, 1H, 2-H)
3r	1097	242 (4.89), 260 sh (4.74), 322 (3.97), 358 (3.91)	1.39 (t, J = 7.2 Hz, 3H, CH ₃), 4.94 (q, J = 7.2 Hz, 2H, CH ₂), 7.04-8.40 (m, 22H, arom-H), 9.24 (d, J = 6.1 Hz, 1H, 2-H)

[a] 2-H/4-H denotes the protons in 2-/4-position and arom-H the other protons of the quinolinium ring and the 2,4,6-triarylphenyl substituent. [b] Mass spectra (FAB): m/z **3a** 448 [C₃₄H₂₆N⁺], **3j** 448 [C₃₄H₂₆N⁺].

salts **1a** [11], **1b** [12], **1c** [13], **1d** [14], **1e** [15], **1f-h** [16] and the thiopyrylium salt **4** [5] were prepared according to literature procedures; the methylquinolinium salts **2a-d** were synthesized applying standard methods for the alkylation of quinolines with dialkyl sulfates [17].

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

Pyrylium perchlorate **1** (5 mmol), quinolinium salt **2** (5 mmol), triethylamine (1.51 g, 15 mmol) and acetic acid (0.60 g, 10 mmol) were heated under reflux in absolute ethanol (40 ml) for 2 hours. The triarylphenylquinolinium perchlorates **3** formed crystallized in some cases from the hot reaction mixture; otherwise their crystallization was initiated by cooling. They were filtered by suction, washed with ethanol and

diethyl ether and recrystallized from acetonitrile.

Synthesis of the 2,4,6-Triphenylphenylquinolinium Perchlorates **3aj** from 2,4,6-Triphenylthiopyrylium Perchlorate (**4**) and the Methylquinolinium Methosulfates **2a,c**.

2,4,6-Triphenylthiopyrylium perchlorate (**4**) (2.12 g, 5 mmol) was reacted with the methylquinolinium methosulfates **2a,c** and triethylamine/acetic acid in ethanol according to the general procedure for the transformation of pyrylium salts **1**. The products formed were isolated and purified as described there. Yields are: **3a** 65%, **3j** 74%; the compounds were identical in all respects with those ones obtained from **1a** and **2a,c**.

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