Ring Transformations of Heterocyclic Compounds. XVII [1]. 2-(2,4,6-Triarylphenyl) Substituted Dihydro-1*H*-imidazolium, Dihydrothiazolium and Thiazolium Salts from 2-Methyl Derivatives by Pyrylium and Thiopyrylium Ring Transformations

Thomas Zimmermann

Institut für Organische Chemie der Universität Leipzig, Permoserstraße 15, D-04303 Leipzig, Germany

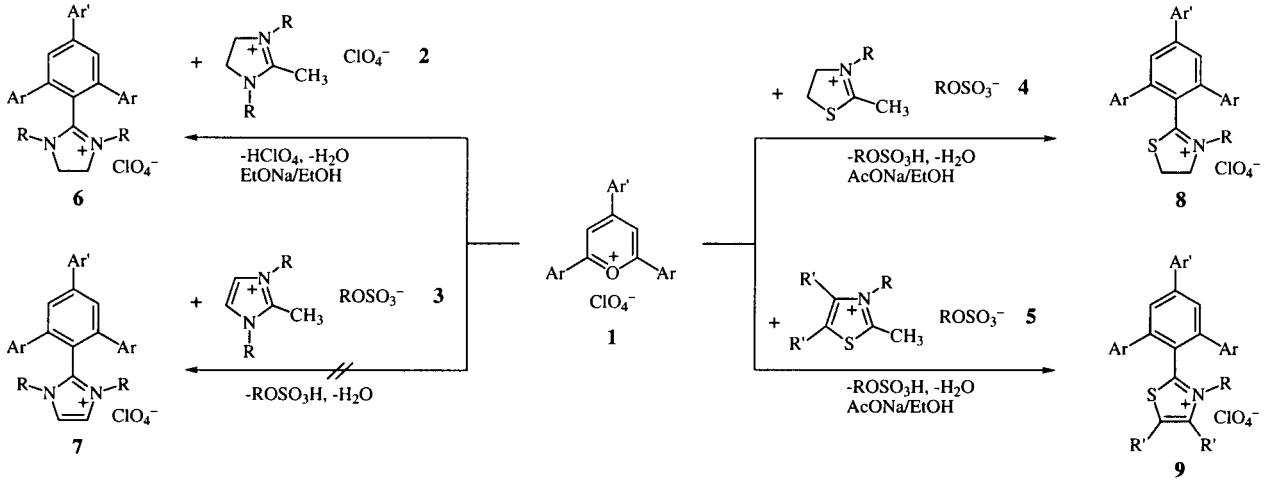
Received January 11, 1999

The synthesis of hitherto unknown 2-(2,4,6-triarylphenyl) substituted 4,5-dihydro-1*H*-imidazolium perchlorates **6**, 4,5-dihydrothiazolium perchlorates **8** and thiazolium perchlorates **9** from their 2-methyl derivatives **2, 4** and **5**, respectively, by a 2,6-[C_5+C] ring transformation of 2,4,6-triarylpyrylium and -thiopyrylium salts **1/10** in ethanol in the presence of an appropriate base (**6**: sodium ethanolate; **8,9**: anhydrous sodium acetate) is reported. Spectroscopic data of the transformation products and structural influences on their formation *via* anhydrobases of the salts **2**, **4** and **5** are discussed.

J. Heterocyclic Chem., **36**, 813 (1999).

Recently aryl substituted heterocyclic compounds have received growing attention as synthetic targets as well as subjects for theoretical investigations resulting from the renaissance of aromatic chemistry initiated by the discovery of fullerenes [2]. In previous papers of this series we described a simple method by which a suitable positioned methyl group of pyridinium [3], bispyridinium [4], quinolinium [5], 1*H*-benzimidazolium [6] and benzothiazolium [6] salts can be converted into the bulky 2,4,6-triarylphenyl substituent by pyrylium [7] and thiopyrylium [8] ring transformations. With methyl substituted 3*H*-indolium [9] and acridinium [1] salts the transformations proceed quite different leading to novel spirocompounds with photochromic properties [10]. These investigations show that i) methyl derivatives of cationic nitrogen heterocycles react in a different, but until now not a predictable way with pyrylium and thiopyrylium salts and ii) further studies on the influence of the structure of these heterocycles on the course of the transformations are necessary.

In this paper we will report on reactions with 4,5-dihydro-1*H*-imidazolium and 4,5-dihydrothiazolium salts as well as their aromatic analogues and compare the results with those earlier obtained for 1*H*-benzimidazolium and benzothiazolium compounds [6] to elucidate the importance of the benzoanellation and the partial saturation of the heterocycles for the transformations.



1	2	4	5	Ar	Ar'	R	R'	6	8	9
a	a	a	a	Ph	Ph	Me	H	a	a	a
b	a	a	a	Ph	4-Me-C_6H_4	Me	H	b	b	b
c	a	a	a	Ph	4-MeO-C_6H_4	Me	H	c	c	c
d	a	a	a	Ph	4-Cl-C_6H_4	Me	H	d	d	d
e	a	a	a	Ph	4-Br-C_6H_4	Me	H	e	e	e
f	a	a	a	4-Me-C_6H_4	Ph	Me	H	f	f	f
g	a	a	a	4-Cl-C_6H_4	Ph	Me	H	g	g	g
h	a	a	a	4-Br-C_6H_4	Ph	Me	H	h	h	h
a	b	b	b	Ph	Ph	Et	H	i	i	i
a			c	Ph	Ph	Me	Me			j

Table 1

Physical and Analytical Data for the 2-(2,4,6-Triarylphenyl) Substituted 4,5-Dihydro-1*H*-imidazolium Perchlorates **6**, 4,5-Dihydrothiazolium Perchlorates **8** and Thiazolium Perchlorates **9**

No.	Perchlorate	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N
6a	1,3-Dimethyl-2-(2,4,6-triphenylphenyl)-4,5-dihydro-1*H*-imidazolium	29	295-296	$C_{29}H_{27}ClN_2O_4$ (503.0)	69.25 69.10	5.41 5.38	5.57 5.63
6b	1,3-Dimethyl-2-[4-(4-methylphenyl)-2,6-diphenylphenyl]-4,5-dihydro-1*H*-imidazolium	32	319-320	$C_{30}H_{29}ClN_2O_4$ (517.0)	69.69 69.73	5.65 5.70	5.42 5.50
6c	2-[4-(4-Methoxyphenyl)-2,6-diphenylphenyl]-1,3-dimethyl-4,5-dihydro-1*H*-imidazolium	30	274-275	$C_{30}H_{29}ClN_2O_5$ (533.0)	67.60 67.80	5.48 5.56	5.26 5.30
6d	2-[4-(4-Chlorophenyl)-2,6-diphenylphenyl]-1,3-dimethyl-4,5-dihydro-1*H*-imidazolium	25	295-296	$C_{29}H_{26}Cl_2N_2O_4$ (537.4)	64.81 64.70	4.88 4.90	5.21 5.30
6e	2-[4-(4-Bromophenyl)-2,6-diphenylphenyl]-1,3-dimethyl-4,5-dihydro-1*H*-imidazolium	25	303-304	$C_{29}H_{26}BrClN_2O_4$ (581.9)	59.86 59.90	4.50 4.52	4.81 4.86
6f	1,3-Dimethyl-2-[2,6-bis(4-methylphenyl)-4-phenylphenyl]-4,5-dihydro-1*H*-imidazolium	15	240-241	$C_{31}H_{31}ClN_2O_4$ (531.1)	70.11 70.12	5.88 5.88	5.28 5.36
6g	2-[2,6-Bis(4-chlorophenyl)-4-phenylphenyl]-1,3-dimethyl-4,5-dihydro-1*H*-imidazolium	18	338-339	$C_{29}H_{25}Cl_3N_2O_4$ (571.9)	60.91 60.97	4.41 4.50	4.90 4.98
6h	2-[2,6-Bis(4-bromophenyl)-4-phenylphenyl]-1,3-dimethyl-4,5-dihydro-1*H*-imidazolium	16	374-375	$C_{29}H_{25}Br_2ClN_2O_4$ (660.8)	52.71 52.79	3.81 3.90	4.24 4.30
6i	1,3-Diethyl-2-(2,4,6-triphenylphenyl)-4,5-dihydro-1*H*-imidazolium	25	307-308	$C_{31}H_{31}ClN_2O_4$ (531.1)	70.11 70.20	5.88 5.96	5.28 5.32
8a	3-Methyl-2-(2,4,6-triphenylphenyl)-4,5-dihydrothiazolium	60	294-295	$C_{28}H_{24}ClNO_4S$ (506.0)	66.46 66.50	4.78 4.86	2.77 2.80
8b	3-Methyl-2-[4-(4-methylphenyl)-2,6-diphenylphenyl]-4,5-dihydrothiazolium	55	275-276	$C_{29}H_{26}ClNO_4S$ (520.1)	66.98 67.03	5.04 5.10	2.69 2.73
8c	2-[4-(4-Methoxyphenyl)-2,6-diphenylphenyl]-3-methyl-4,5-dihydrothiazolium	56	266-267	$C_{29}H_{26}ClNO_5S$ (536.1)	64.98 64.90	4.89 4.81	2.61 2.58
8d	2-[4-(4-Chlorophenyl)-2,6-diphenylphenyl]-3-methyl-4,5-dihydrothiazolium	49	264-265	$C_{28}H_{23}Cl_2NO_4S$ (540.5)	62.23 62.30	4.29 4.36	2.59 2.61
8e	2-[4-(4-Bromophenyl)-2,6-diphenylphenyl]-3-methyl-4,5-dihydrothiazolium	61	285-286	$C_{28}H_{23}BrClNO_4S$ (584.9)	57.50 57.59	3.96 4.01	2.39 2.46
8f	3-Methyl-2-[2,6-bis(4-methylphenyl)-4-phenylphenyl]-4,5-dihydrothiazolium	53	294-295	$C_{30}H_{28}ClNO_4S$ (534.1)	67.47 67.53	5.28 5.38	2.62 2.62
8g	2-[2,6-Bis(4-chlorophenyl)-4-phenylphenyl]-3-methyl-4,5-dihydrothiazolium	51	327-328	$C_{28}H_{22}Cl_3NO_4S$ (574.9)	58.50 58.60	3.86 3.94	2.44 2.46
8h	2-[2,6-Bis(4-bromophenyl)-4-phenylphenyl]-3-methyl-4,5-dihydrothiazolium	74	327-328	$C_{28}H_{22}Br_2ClNO_4S$ (663.8)	50.66 50.68	3.34 3.40	2.11 2.20
8i	3-Ethyl-2-(2,4,6-triphenylphenyl)-4,5-dihydrothiazolium	51	255-256	$C_{29}H_{26}ClNO_4S$ (520.1)	66.98 67.00	5.04 5.20	2.69 2.75
9a	3-Methyl-2-(2,4,6-triphenylphenyl)thiazolium	67	239-240	$C_{28}H_{22}ClNO_4S$ (504.0)	66.73 66.61	4.40 4.38	2.78 2.85
9b	3-Methyl-2-[4-(4-methylphenyl)-2,6-diphenylphenyl]thiazolium	56	252-253	$C_{29}H_{24}ClNO_4S$ (518.0)	67.24 67.10	4.67 4.70	2.70 2.75
9c	2-[4-(4-Methoxyphenyl)-2,6-diphenylphenyl]-3-methylthiazolium	56	144-145 [a] 224-225 [a]	$C_{29}H_{24}ClNO_5S$ (534.0)	65.22 65.40	4.53 4.53	2.62 2.65
9d	2-[4-(4-Chlorophenyl)-2,6-diphenylphenyl]-3-methylthiazolium	48	201-202 [a] 225-226 [a]	$C_{28}H_{21}Cl_2NO_4S$ (538.5)	62.46 62.51	3.93 3.96	2.60 2.68
9e	2-[4-(4-Bromophenyl)-2,6-diphenylphenyl]-3-methylthiazolium	65	259-260	$C_{28}H_{21}BrClNO_4S$ (582.9)	57.70 57.81	3.63 3.70	2.40 2.42
9f	3-Methyl-2-[2,6-bis(4-methylphenyl)-4-phenylphenyl]thiazolium	79	263-264	$C_{30}H_{26}ClNO_4S$ (532.1)	67.72 67.80	4.93 4.95	2.63 2.64
9g	2-[2,6-Bis(4-chlorophenyl)-4-phenylphenyl]-3-methylthiazolium	75	295-296	$C_{28}H_{20}Cl_3NO_4S$ (572.9)	58.70 58.72	3.52 3.56	2.44 2.40
9h	2-[2,6-Bis(4-bromophenyl)-4-phenylphenyl]-3-methylthiazolium	68	272-273	$C_{28}H_{20}Br_2ClNO_4S$ (661.8)	50.82 50.78	3.05 3.00	2.11 2.08
9i	3-Ethyl-2-(2,4,6-triphenylphenyl)thiazolium	80	232-233	$C_{29}H_{24}ClNO_4S$ (518.0)	67.24 67.18	4.67 4.83	2.70 2.70
9j	3,4,5-Trimethyl-2-(2,4,6-triphenylphenyl)-thiazolium	62	324-325	$C_{30}H_{26}ClNO_4S$ 532.1	67.72 67.85	4.93 4.94	2.63 2.70

[a] Double melting point.

When the 2,4,6-triarylpyrylium perchlorates **1a-h** were refluxed with the 1,3-dialkyl-2-methyl-4,5-dihydro-1*H*-imidazolium perchlorates **2a,b** and sodium ethanolate in ethanol the 1,3-dialkyl-2-(2,4,6-triarylphenyl)-4,5dihydro-

Table 2
Spectral Data for the 2-(2,4,6-Triarylphenyl) Substituted 4,5-Dihydro-1*H*-imidazolium Perchlorates **6**, 4,5-Dihydrothiazolium Perchlorates **8** and Thiazolium Perchlorates **9**

Compound	IR (potassium bromide) (cm^{-1}) ClO_4	UV (acetonitrile) λ_{max} (nm) (log ε)	^{1}H-NMR (dimethyl-d_6 sulfoxide) [a] δ (ppm)
6a [b], [c]	1094	250 (4.67)	2.52 (s, 6H, NCH_3), 3.60 (s, 4H, CH_2), 7.39-7.90 (m, 17H, arom-H)
6b	1095	225 sh (4.48), 253 (4.61), 284 sh (4.37)	2.53 (s, 3H, CH_3), 2.51 (s, 6H, NCH_3), 3.58 (s, 4H, CH_2), 7.27-7.87 (m, 16H, arom-H)
6c	1091	226 sh (4.56), 256 (4.53), 293 (4.42)	2.51 (s, 6H, NCH_3), 3.58 (s, 4H, CH_2), 3.77 (s, 3H, OCH_3), 7.00-7.88 (m,16H, arom-H)
6d	1094	252 (4.68), 282 sh (4.41)	2.52 (s, 6H, NCH_3), 3.59 (s, 4H, CH_2), 7.37-7.98 (m, 16H, arom-H)
6e	1095	252 (4.68), 281 sh (4.47)	2.53 (s, 6H, NCH_3), 3.59 (s, 4H, CH_2), 7.37-7.92 (m, 16H, arom-H)
6f	1095	255 (4.74)	2.35 (s, 6H, CH_3), 2.52 (s, 6H, NCH_3), 3.61 (s, 4H, CH_2), 7.25-7.88 (m, 14H, arom-H)
6g	1095	255 (4.76)	2.57 (s, 6H, NCH_3), 3.65 (s, 4H, CH_2), 7.39-7.93 (m, 14H, arom-H)
6h	1096	256 (4.76)	2.57 (s, 6H, NCH_3), 3.66 (s, 4H, CH_2) 7.33-7.93 (m, 14H, arom-H)
6i	1095	250 (4.69)	0.50 (t, 6H, CH_3), 3.04 (q, 4H, NCH_2), 3.66 (s, 4H, CH_2), 7.37-7.91 (m, 17H, arom-H)
8a [b],[c]	1095	245 (4.57), 302 (4.18)	2.92 (s, 3H, NCH_3), 3.47 (t, J = 9.2 Hz, 2H, 5-H), 4.19 (t, J = 9.2 Hz, 2H, 4-H), 7.41-7.86 (m, 17H, arom-H)
8b	1093	243 (4.56), 310 (4.24)	2.30 (s, 3H, CH_3), 2.91 (s, 3H, NCH_3), 3.45 (t, J = 9.0 Hz, 2H, 5-H), 4.17 (t, J = 9.0 Hz, 2H, 4-H), 7.25-7.82 (m, 16H, arom-H)
8c	1095	238 (4.53), 273 sh (4.29), 324 (4.22)	2.91 (s, 3H, NCH_3), 3.44 (t, J = 9.0 Hz, 2H, 5-H), 3.76 (s, 3 H, OCH_3), 4.16 (t, J = 9.0 Hz, 2H, 4-H), 6.99-7.85 (m, 16H, arom-H)
8d	1095	247 (4.58), 300 (4.26)	2.93 (s, 3H, NCH_3), 3.47 (t, J = 9.0 Hz, 2H, 5-H), 4.19 (t, J = 9.0 Hz, 2H, 4-H), 7.44-7.93 (m, 16H, arom-H)
8e	1091	249 (4.57), 302 (4.28)	2.93 (s, 3H, NCH_3), 3.46 (t, J = 9.0 Hz, 2H, 5-H), 4.18 (t, J = 9.0 Hz, 2H, 4-H), 7.43-7.87 (m, 16H, arom-H)
8f	1093	252 (4.62), 303 sh (4.17)	2.35 (s, 6H, CH_3), 2.92 (s, 3H, NCH_3), 3.48 (t, J = 9.1 Hz, 2H, 5-H), 4.20 (t, J = 9.1 Hz, 2H, 4-H), 7.33-7.86 (m, 15 H, arom-H)
8g	1092	250 (4.63), 304 sh (4.19)	2.98 (s, 3H, NCH_3), 3.52 (t, J = 9.1 Hz, 2H, 5-H), 4.25 (t, J = 9.1 Hz, 2H, 4-H), 7.42-7.88 (m, 15H, arom-H)
8h	1091	251 (4.65), 301 sh (4.19)	2.98 (s, 3H, NCH_3), 3.52 (t, J = 9.1 Hz, 2H, 5-H), 4.25 (t, J = 9.1 Hz, 2H, 4-H), 7.39-7.87 (m, 15H, arom-H)
8i	1094	246 (4.60), 301 (4.20)	0.53 (t, 3H, CH_3), 3.42-3.54 (m, 4H, 5-H + NCH_2), 4.22 (t, J = 8.9 Hz, 2H, 4-H), 7.44-7.89 (m, 17H, arom-H)
9a [b],[c]	1100	245 (4.60), 306 (4.16)	3.55 (s, 3H, NCH_3), 7.23-7.90 (m, 17H, arom-H), 8.28 (d, J = 3.9 Hz, 1H, 4-H), 8.31 (d, J = 3.9 Hz, 1H, 5-H)
9b	1101	245 (4.59), 309 (4.25)	2.32 (s, 3H, CH_3), 3.53 (s, 3H, NCH_3), 7.23-7.89 (m, 16H, arom-H), 8.17 (d, J = 3.8 Hz, 1H, 4-H), 8.20 (d, J = 3.8 Hz, 1H, 5-H)
9c	1096	243 (4.52), 272 sh (4.29), 319 (4.26)	3.53 (s, 3H, NCH_3), 3.77 (s, 3H, OCH_3), 7.01-7-89 (m, 16H, arom-H), 8.17 (d, J = 3.9 Hz, 1H, 4-H), 8.20 (d, J = 3.9 Hz, 1H, 5-H)
9d	1094	246 (4.59), 305 (4.23)	3.54 (s, 3H, NCH_3), 7.23-7.98 (m, 16H, arom-H), 8.18 (d, J = 4.0 Hz, 1H, 4-H), 8.21 (d, J = 4.0 Hz, 1H, 5-H)
9e	1095	247 (4.58), 305 (4.25)	3.54 (s, 3H, NCH_3), 7.23-7.93 (m, 16H, arom-H), 8.18 (d, J = 3.9 Hz, 1H, 4-H), 8.21 (d, J = 3.9 Hz, 1H, 5-H)
9f	1119	250 (4.62), 308 (4.11)	2.26 (s, 6H, CH_3), 3.53 (s, 3H, NCH_3), 7.14-7.90 (m, 15H, arom-H), 8.13 (d, J = 4.0 Hz, 1H, 4-H), 8.22 (d, J = 4.0 Hz, 1H, 5-H)
9g	1092	249 (4.65), 306 (4.18)	3.58 (s, 3H, NCH_3), 7.27-7.94 (m, 15H, arom-H), 8.22 (d, J = 3.8 Hz, 1H, 4-H), 8.25 (d, J = 3.8 Hz, 1H, 5-H)
9h	1095	250 (4.68), 305 (4.20)	3.58 (s, 3H, NCH_3), 7.20-7.93 (m, 15H, arom-H), 8.22 (d, J = 3.9 Hz, 1H, 4-H), 8.25 (d, J = 3.9 Hz, 1H, 5-H)
9i	1094	245 (4.63), 303 (4.19)	0.82 (t, 3H, CH_3), 3.92 (q, 2H, CH_2), 7.22-7.91 (m, 17H, arom-H), 8.28 (d, J = 4.0 Hz, 1H, 4-H), 8.35 (d, J = 4.0 Hz, 1H, 5-H)
9j	1094	247 (4.60), 308 (4.25)	2.20 (s, 3H, 4-CH_3), 2.93 (s, 3H, 5-CH_3), 3.42 (s, 3H, NCH_3), 7.21-7.88 (m, 17H, arom-H)

[a] 4-H and 5-H denote the protons in 4-and 5-position, respectively, and arom-H the protons bonded to the benzene rings. [b] ^{13}C nmr **6a** 31.7 (NCH_3), 47.5 (CH_2), 114.9, 125.4, 126.0, 126.1, 126.9, 127.1, 127.2, 135.8, 136.0, 140.9, 142.8 (carbons of the benzene rings) 162.6 (C-2), **8a**, 29.2 (NCH_3), 59.1 (CH_2), 119.1, 125.6, 126.4, 126.6, 127.1, 127.2, 127.3, 136.0, 136.3, 140.5, 143.0 (carbons of the benzene rings), 186.2 (C-2), **9a** 38.0 (NCH_3), 118.5, 125.3, 125.4, 126.1, 126.3, 126.5, 126.8, 127.2, 135.5, 136.0 136.3, 142.0, 142.6 (carbons of the benzene rings, C-4 and C-5 of the thiazole), 167.1 (C-2). [c] Mass spectra (FAB): m/z **6a** 403 [$C_{29}H_{27}N_2^+$], **8a** 406 [$C_{28}H_{24}NS^+$], **9a** 404 [$C_{28}H_{22}NS^+$].

1*H*-imidazolium derivatives **6a-i** were obtained (*cf.* Table 1). Although the yields were only moderate the procedure is a valuable synthetic method since it can easily be scaled up and the products formed in high purity represent novel 4,5-dihydro-1*H*-imidazolium salts with a bulky substituent at C-2.

Efforts to extend the reactions to the 1,3-dialkyl-2-methyl-1*H*-imidazolium salts **3**, the dehydrogenated analogues of **2**, were unsuccessful. From the reaction mixtures obtained by heating of the pyrylium salts **1** with **3** and sodium ethanolate in ethanol no transformation products of the type **7** could be isolated. The same was true when the sodium ethanolate was substituted by another condensing agent such as triethylamine, triethylamine/acetic acid, sodium acetate or piperidine acetate applied with high efficiency for related pyrylium ring transformations [1,4-6,13,14].

In contrast to the azolium compounds **2/3** the 3-alkyl-2-methyl-4,5-dihydrothiazolium salts **4a,b** as well as their aromatic analogues, the 3-alkyl-2-methylthiazolium salts **5a-c**, reacted smoothly with the pyrylium perchlorates **1a-h** in the presence of anhydrous sodium acetate in boiling ethanol to give the former unknown 2-(2,4,6-triarylphenyl) derivatives **8a-i** and **9a-j**, respectively. The yields (**8a-h**: 49-74%, **9a-j**: 48-80%) were comparable to those obtained for 3-alkyl-2-methylbenzothiazolium salts (34-65% [6]).

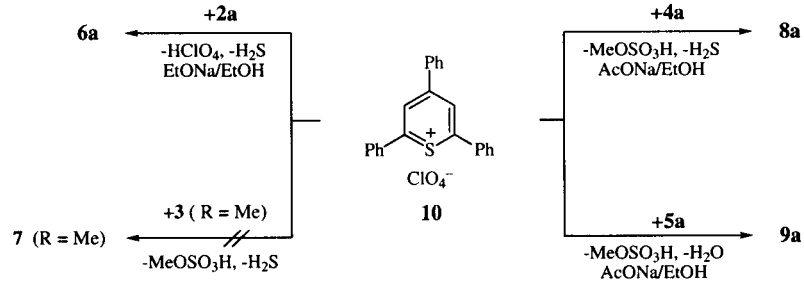
In all the transformations the precipitation of the products as mixtures of salts with different anions was avoided by using pyrylium and methylazolium salts with the same anion (*e.g.* ClO_4^-) or by selecting such a combination of anions (*e.g.* $ROSO_3^-$, R = alkyl and ClO_4^-) in which only one is capable to form a low soluble salt with the 2-(2,4,6-triarylphenyl)azolium cation.

To explore the behaviour of the 2,4,6-triarylthiopyrylium salts which differ from the pyrylium compounds **1** only by the kind of the heteroatom, the reaction of 2,4,6-triphenylthiopyrylium perchlorate (**10**) with the azolium salts **2a, 3** (R = Me), **4a** and **5a** were studied as representative examples under the conditions applied in the pyrylium series. The products **6a, 8a** and **9a** obtained were identical in all respects with those ones formed from the pyrylium salt **1a** whereas **3** (R = Me) also failed to react. Since 2,4,6-triarylthiopyrylium salts have to be prepared by heteroatom exchange from the related pyrylium salts **1** with sodium sulphide in acetone according to the Wizinger method [15] and the yield and purity are lower it becomes evident that the direct synthesis from **1** is more convenient and effective.

One may assume that in the course of the pyrylium and thiopyrylium ring transformations the methyl substituted nitrogen heterocycles were deprotonated to the corresponding anhydrobases [16] attacking the pyrylium/thiopyrylium cations of **1/10** as carbon nucleophiles of the enamine type in the preferred position 2 [7,8]. Then *via* ring opening/ring closure a new benzene ring is built up from five carbon atoms of **1/10** the C-atom of the 2-methyl group of **2, 4** and **5**, respectively, which connects the former positions 2 and 6 of **1/10**. Hence, the reactions can be classified as 2,6-[C_5+C]-transformations [17].

A comparison of the transformations described and the reactions of the pyrylium and thiopyrylium perchlorates **1/10** with 1-alkyl-2-methyl-1*H*-benzimidazolium and 3-alkyl-2-methylbenzothiazolium salts [6] provides valuable information on the role played by the anellated benzene ring and the influence of the degree of unsaturation of the nitrogen heterocycles. Whereas in the case of the thiazolium compounds the presence of the anellated benzene ring or the degree of saturation have practically no influence on the yields of transformation products the benzoanellation or (in a smaller extend) a partial saturation of the imidazolium system are crucial prerequisites for a successful transformation.

The results of the elemental analyses and the spectroscopic data (*cf.* Tables 1 and 2) strongly support the structure proposed for the 2-(2,4,6-triarylphenyl) substituted azolium perchlorates **6, 8** and **9**. In the ^1H nmr spectra the *N*-bonded methyl group shows the expected singlet which is localized in the case of the partially saturated compounds at 2.51-2.57 ppm (**6a-h**) and 2.91-2.98 ppm (**8a-h**). The presence of the aromatic heterocyclic system in **9** causes a significant downfield shift of the *N*-methyl protons (**9a-h:** 3.42-3.58 ppm). The CH_2-groups of **6** are responsible for the singlet at 3.58-3.66 ppm whereas the magnetically not equivalent methylene protons at C-4 and C-5 of **8** causes signals at 3.42-3.54 ppm and 4.16-4.25 ppm splitted by coupling to triplets. The multiplet at 6.99-7.98 ppm of the protons bonded at the phenyl rings is accompanied in the case of the thiazolium salts **9a-i** by two doublets at 8.17-8.35 ppm. NOe experiments clearly showed that the irradiation at the



N-methyl singlet causes a signal enhancement of the doublet at higher field but not of the doublet at lower field indicating that the first one is caused by the proton at C-4 and the latter one by the proton at C-5. In the same way the singlets at 2.20 ppm and 2.93 ppm of the 4,5-dimethyl substituted thiazolium salt **9j** can be attributed to the 4- and 5-methyl group, respectively. A characteristic feature of the ^{13}C nmr spectra, recorded for **6a, 8a** and **9a**, is besides the signals of the aliphatic carbons and the C-atoms of the benzene rings the signal of C-2 at 162.6 ppm (**6a**), 186.2 ppm (**8a**) and 167.1 ppm (**9a**). Its appearance at the lowest field is in accordance with the high electron deficiency at this carbon atom. The FAB mass spectra of **6a, 8a** and **9a** show exactly the mass peaks of the corresponding cations. In the uv spectra a strong absorption band at 238-256 nm can be observed which is accompanied in the case of the dihydrothiazolium and thiazolium salts **8/9** by a second band of lower intensity at 300-324 nm. The results of the elemental analyses and the characteristic perchlorate absorption [18] at 1090-1119 cm^{-1} indicate that the transformation products were obtained as perchlorate salts.

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ^1H nmr and ^{13}C nmr spectra were recorded on a Varian Gemini 200 spectrometer (^1H: 199.975 MHz, ^{13}C: 50.289 MHz) and on a Varian Gemini 2000 spectrometer (^1H: 200.041 MHz, ^{13}C: 50.305 MHz) in dimethyl-d_6 sulfoxide at 25° with hexamethyl disiloxane as internal standard, ir spectra were obtained on a ATI Mattson Genesis FTIR spectrophotometer (in potassium bromide) and uv spectra on a Zeiss M 40 instrument (acetonitrile, 25°). Mass spectra were determined on a Finnigan MAT 701 A spectrometer (FAB, **8** keV, argon, matrix: nitrobenzyl alcohol). The pyrylium perchlorates **1a** [19], **1b** [20], **1c** [21], **1d** [22], **1e** [23], **1f-h** [24], the thiopyrylium perchlorate **10** [15], 2-methylthiazole [25] and the azolium salts **3** (R = Me) [26], **4a** [27], **5a** [28] were prepared by literature procedures. *N,N'*-Dimethylethylenediamine, *N,N'*-diethylethylenediamine, triethyl orthoacetate, 2-methyl-4,5-dihydrothiazole and 2,4,5-trimethylthiazole were purchased from Aldrich.

Preparation of the *N*-Alkyl Substituted 2-Methylazolium Salts **2a,b, 4b** and **5b,c**.

1,2,3-Trimethyl-4,5-dihydro-1*H*-imidazolium Perchlorate (**2a**).

This perchlorate was prepared by a modification of the procedure reported for the synthesis of the related tetrafluoroborate [29].

N,N'-Dimethylethylenediamine (1.76 g, 20 mmoles), triethyl orthoacetate (3.24 g, 20 mmoles) and ammonium chloride (1.07 g, 20 mmoles) were magnetically stirred in a destillation apparatus at 120° for 3 hours at atmospheric pressure and 2 hours *in vacuo*. The distillate formed was discarded and the solid residue in the destillation flask was dissolved in 20 ml of absolute ethanol. Perchloric acid (70% solution in water, 2.87 g, 20 mmoles) was added dropwise under magnetic stirring. The crystalline precipitate obtained was filtered by suction, washed with ethanol and ether and dried to give 3.69 g (87%) 1,2,3-trimethyl-4,5-dihydro-1*H*-imidazolium perchlorate (**2a**) which was used without further purification. A specimen recrystallized from acetonitrile/ether melted at 245-246° (lit 242-244° [30]).

1,3-Diethyl-2-methyl-4,5-dlhydro-1*H*-imidazolium Perchlorate (**2b**).

This compound was prepared according to the procedure given for the synthesis of **2a** from *N,N'*-diethylethylenediamine (2.32 g, 20 mmoles), triethyl orthoacetate, ammonium chloride and perchloric acid, yield 3.47 g (72%), mp 164-166° (acetonitrile, ether); ^1H nmr: δ ppm 1.09 (t, 3H, CH_3), 2.19 (s, 3H, 2-CH_3), 3.40 (q, 2H, NCH_2), 3.75 (s, 4H, 4-H + 5-H).

Anal. Calcd. for $C_8H_{17}ClN_2O_4$: C, 39.92; H, 7.12; N, 11.64. Found: C, 39.93; H, 7.06; N, 11.50.

3-Ethyl-2-methyl-4,5-dihydrothiazolium Ethosulfate (**4b**).

2-Methyl-4,5-dihydrothiazole (2.53 g, 25 mmoles) and diethyl sulfate (3.85 g, 25 mmoles) in 10 ml of xylene were magnetically stirred at 90° for 30 minutes. The 3-ethyl-2-methyl-4,5-dihydrothiazolium ethosulfate (**4b**) was obtained as an brown oil which was separated from the reaction mixture after cooling by decantation. Dry ether (20 ml) was added, the flask was intensively shaken and the etheral layer was decanted. After twofold repetition of this washing procedure solvent residues were removed *in vacuo*. The crude hygroscopic product was used without further purification, yield 4.60 g (82%).

3-Ethyl-2-methylthiazolium Ethosulfate (**5b**).

This compound was prepared as described for **4b** from 2-methylthiazole (2.48 g, 25 mmoles) and diethyl sulfate (3.85 g, 25 mmoles), yield 4.78 g (76%), hygroscopic yellow oil which formed a semi-solid mass after longer standing at room temperature; used without further purification.

2,3,4,5-Tetramethylthiazolium Methosulfate (**5c**).

This compound was synthesized according to the procedure given for the preparation of **4b** from 2,4,5-trimethylthiazole (3.18 g, 25 mmoles) and dimethyl sulfate (3.15 g, 25 mmoles), yield 5.80 g (92%), hygroscopic, nearly colourless crystals; used without further purification.

Preparation of 2-(2,4,6-Triarylphenyl) Substituted 4,5-Dihydro-1*H*-imidazolium Perchlorates **6** from 2,4,6-Triarylpyrylium Perchlorates **1** and 2-Methyl-4,5-dihydro-1*H*-imidazolium Salts **2**. General Procedure (*cf.* Tables 1 and 2).

Sodium metal (0.35 g, 15 mmoles) was dissolved in absolute ethanol (30 ml). After addition of 5 mmoles of the pyrylium perchlorate **1** and 5 mmoles of the 2-methyl-4,5-dihydro-1*H*-imidazolium salt **2** the reaction mixture was heated under refluxed for 4 hours. The 2-(2,4,6-triarylphenyl)-4,5-dihydro-1*H*-imidazolium perchlorates **6** formed crystallized in the most cases from the hot reaction mixture. Otherwise their crystallization was initiated by cooling. They were filtered off by suction, washed with water, ethanol and ether and purified by dissolving in a minimal amount of hot acetonitrile and subsequent precipitation with ether.

Preparation of 2-(2,4,6-Triarylphenyl) Substituted 4,5-Dihydrothiazolium Perchlorates **8** and Thiazolium Perchlorates **9** from 2,4,6-Triarylpyrylium Perchlorates **1** and 2-Methyl-4,5-dihydrothiazolium/2-Methylthiazolium Salts **4/5**. General Procedure (*cf.* Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles of pyrylium perchlorate **1**, 5 mmoles of 2-methyl-4,5-dihydrothiazolium or 2-methylthiazolium

salt **4/5** and anhydrous sodium acetate (1.23 g, 15 mmoles) were added. The reaction mixture was then refluxed for 2 hours. During this time the 2-(2,4,6-triarylphenyl)-4,5-dihydrothiazolium and thiazolium perchlorates **8/9** usually separated as crystalline solids. In some cases cooling of the reaction mixture was necessary to initiate the crystallization. The products were isolated and purified as described for the 4,5-dihydro-1*H*-imidazolium perchlorates **6**.

Attempted Synthesis of 1,3-Dimethyl-2-(2,4,6-triphenylphenyl)-1*H*-imidazolium Perchlorate (**7**, R = Me, Ar = Ar' = Ph) from 2,4,6-Triphenylpyrylium Perchlorate (**1a**) and 1,2,3-Trimethyl-1*H*-imidazolium Methosulfate (**3**, R = Me).

According to the general procedures given above 2,4,6-triphenylpyrylium perchlorate (**1a**) (2.04 g, 5 mmoles) and 1,2,3-trimethyl-1*H*-imidazolium methosulfate (**3**, R = Me) (1.11 g, 5 mmoles) were reacted. The crystalline precipitates obtained were analyzed by nmr spectroscopy. They contained unreacted starting materials; no transformation product of the type **3** could be detected. Changing the base sodium ethanolate or sodium acetate by equimolar amounts of triethylamine, triethylamine/acetic acid or piperidine acetate gave the same results.

Synthesis of the 2-(2,4,6-Triphenylphenyl) Substituted Azolium Perchlorates **6a, 8a** and **9a** from 2,4,6-Triphenylthiopyrylium Perchlorate (**10**) and the Methyl Derivatives **2a, 4a** and **5a**.

2,4,6-Triphenylthiopyrylium perchlorate (**10**) (2.12 g, 5 mmoles) was reacted with 1,2,3-trimethyl-4,5-dihydro-1*H*-imidazolium perchlorate (**2a**), 2,3-dimethyl-4,5-dihydrothiazolium methosulfate (**4a**) and 2,3-dimethylthiazolium methosulfate (**5a**) as described in the general procedures; yields: **6a**: 6%, **8a**: 36%, **9a**: 64%; the compounds were identical in all respects with those ones obtained from **1a** and **2a, 4a** and **5a**, respectively.

With 1,2,3-trimethyl-1*H*-imidazolium methosulfate (**3**, R = Me) and **10** no formation of any transformation products was observed.

Acknowledgement.

The financial support by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie is gratefully appreciated.

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