Ring Transformations of Heterocyclic Compounds. XIV [1]. Ring Transformations of Pyrylium and Thiopyrylium Salts with Anhydrobases Derived from 1*H*-Benzimidazolium and Benzothiazolium Salts: An Easy Access to 2-(2,4,6-Triarylphenyl) 1*H*-Benzimidazolium and Benzothiazolium Derivatives

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The preparation of former unknown 2-(2,4,6-triarylphenyl) substituted 1*H*-benzimidazolium perchlorates **7** and benzothiazolium perchlorates **8** from 2-methyl substituted derivatives **5/6** by a 2,6-[C_5+C] ring transformation of 2,4,6-triarylpyrylium and 2,4,6-triarylthiopyrylium salts **1/9** in the presence of an appropriate base (**7**: sodium ethoxide, **8**: sodium acetate) is reported. Spectroscopic data of the transformation products and their mode of formation *via* anhydrobases of the salts **5/6** are discussed.

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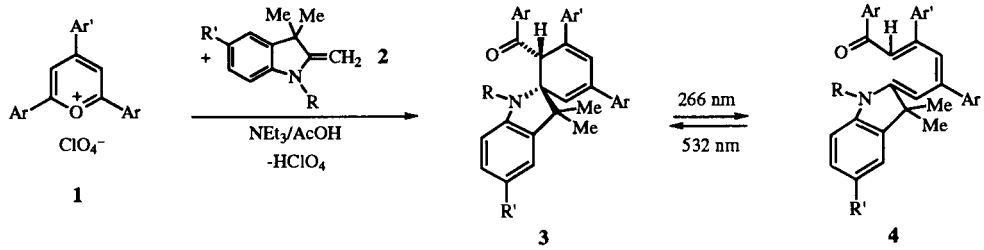
In a previous paper of this series we described the first ring transformation reactions of pyrylium [2] and thiopyrylium [3] salts with heterocyclic anhydrobases of the enamine type [4]. These transformations offer a simple method for the conversion of a methyl group in 2-/4-position of pyridinium and quinolinium salts into a 2,4,6-triarylphenyl residue [4,5]. Such highly aryl substituted heterocycles seem to be interesting molecules for studying through space interactions between aromatic π-systems since the aryl substituents are twisted out of plane and arranged approximately face to face with the heterocyclic ring.

Extending the pyrylium ring transformations to anhydrobases of five-membered benzene condensed heterocycles we made a surprising observation. When 2,4,6-triarylpyrylium salts **1** were treated with 3,3-dimethyl-2-methyleneindolines **2** (R = Me, Ph; R' = H, Cl, Br, NO_2), which are anhydrobases of 2,3,3-trimethyl-3*H*-indolium salts, former unknown 6-aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-indolines] **3** were obtained in high yield and diastereoselectivity [6]. These compounds represent a novel class of photochromic substances [7]. By uv irradiation an electrocyclic ring opening to colored merocyanines **4** was observed; the acyclic valence isomers could be recyclized with visible light to the starting compounds **3**.

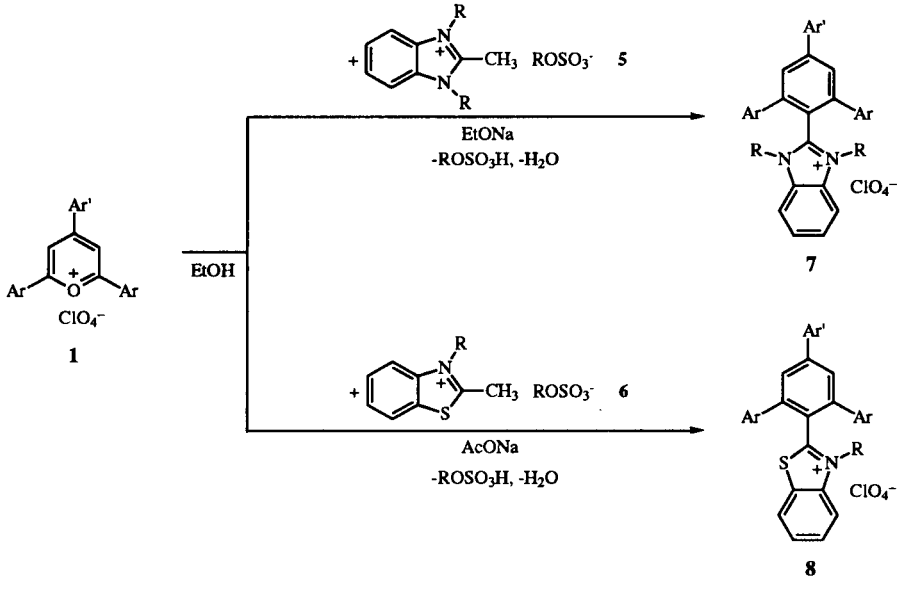
Thus, we became interested in the study of transformations of the salts **1** with anhydrobases of the enamine type derived from other five-membered benzene condensed heterocycles. In this paper we wish to report on our results obtained with anhydrobases of 1*H*-benzimidazolium [8] and benzothiazolium salts [9]. In principle with these compounds two reaction paths are possible. The first one should give 2-(2,4,6-triarylphenyl)-1*H*-benzimidazolium and benzothiazolium salts, respectively, by conversion of a 2-positioned methyl group into a 2,4,6-triarylphenyl substituent and the second one should lead to benzimidazol or benzothiazol derivatives with a cyclohexadiene ring, *spiro* condensed at the carbon atom in position 2. The experiments clearly showed that the transformations followed the first path.

When the 2,4,6-triarylpyrylium perchlorates **1** and the 2-methyl-1*H*-benzimidazolium salts **5** were refluxed in absolute ethanol in the presence of an appropriate base the 2-(2,4,6-triarylphenyl)-1*H*-benzimidazolium perchlorates **7** in yields up to 73% were formed. Under the same conditions from the 2,4,6-triarylpyrylium perchlorates **1** and the 2-methylbenzothiazolium salts **6** the 2-(2,4,6-triarylphenyl)benzothiazolium perchlorates **8** were obtained (yield 34-65%). For the first reaction sodium ethoxide



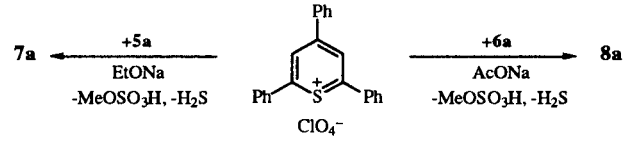
was advantageously used as base, whereas anhydrous sodium acetate gave the best results in the case of the second one. The transformation products **7/8** represent 1*H*-benzimidazolium and benzothiazolium compounds with a hitherto unknown substitution pattern.

zolium and benzothiazolium derivatives **7/8** *via* the pyrylium route, since the thiopyrylium salts have to be prepared from the corresponding pyrylium salts by heteroatom exchange according to the Wizinger procedure [10].



1	5	6	Ar	Ar'	R	7	8
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	Et	**i**	
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	Et		**i**

Further experiments showed that the ring transformations observed for the pyrylium salts **1** also worked well in the thiopyrylium series. When the 2,4,6-triphenylthiopyrylium perchlorate (**9**) was treated with 1,2,3-trimethyl-1*H*-benzimidazolium methosulfate (**5a**) and sodium ethoxide or 2,3-dimethylbenzothiazolium methosulfate (**6a**) and sodium acetate in ethanol the 2-(2,4,6-triphenylphenyl) substituted 1*H*-benzimidazolium perchlorate **7a** and the benzothiazolium perchlorate **8a**, respectively, could be isolated. Although the yields were in the same region as for the analogous reactions of the pyrylium salts it is more convenient to synthesize the 2-(2,4,6-triarylphenyl)-1*H*-benzimida-



The formation of the transformation products **7/8** can be explained in close analogy to other reactions of the pyrylium and thiopyrylium salts **1/9** with heterocyclic anhydrobases of the enamine type [1,4-6]. Under the action of base the 1*H*-benzimidazolium and benzothiazolium salts **5/6** are deprotonated to the corresponding

Table 1

Physical and Analytical Data for the 2-(2,4,6-Triarylphenyl)-1*H*-benzimidazolium Perchlorates **7** and for the 2-(2,4,6-Triarylphenyl)benzothiazolium Perchlorates **8**

No.	Perchlorate	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N
7a	1,3-Dimethyl-2-(2,4,6-triphenylphenyl)-1*H*-benzimidazolium	46	305-306	$C_{33}H_{27}ClN_2O_4$ (551.1)	71.93 71.73	4.94 5.10	5.08 5.00
7b	1,3-Dimethyl-2-[4-(4-methylphenyl)-2,6-diphenylphenyl]-1*H*-benzimidazolium	50	311-312	$C_{34}H_{29}ClN_2O_4$ (565.1)	72.27 72.40	5.17 5.20	4.96 5.15
7c	2-[4-(4-Methoxyphenyl)-2,6-diphenylphenyl]-1,3-dimethyl-1*H*-benzimidazolium	41	294-295	$C_{34}H_{29}ClN_2O_5$ (581.1)	70.28 70.10	5.03 5.12	4.82 4.90
7d	2-[4-(4-Chlorophenyl)-2,6-diphenylphenyl]-1,3-dimethyl-1*H*-benzimidazolium	43	323-325	$C_{33}H_{26}Cl_2N_2O_4$ (585.5)	67.70 67.64	4.48 4.53	4.78 4.70
7e	2-[4-(4-Bromophenyl)-2,6-diphenylphenyl]-1,3-dimethyl-1*H*-benzimidazolium	61	335-337	$C_{33}H_{26}BrClN_2O_4$ (630.0)	62.92 63.00	4.16 4.30	4.45 4.60
7f	1,3-Dimethyl-2-[2,6-bis(4-methylphenyl)-4-phenylphenyl]-1*H*-benzimidazolium	73	311-313	$C_{35}H_{31}ClN_2O_4$ (579.1)	72.59 72.50	5.40 5.59	4.84 4.90
7g	2-[2,6-Bis(4-chlorophenyl)-4-phenylphenyl]-1,3-dimethyl-1*H*-benzimidazolium	42	334-336	$C_{33}H_{25}Cl_3N_2O_4$ (619.9)	63.94 63.95	4.06 4.20	4.52 4.60
7h	2-[2,6-Bis(4-bromophenyl)-4-phenylphenyl]-1,3-dimethyl-1*H*-benzimidazolium	38	335-337	$C_{33}H_{25}Br_2ClN_2O_4$ (708.9)	55.92 56.00	3.55 3.60	3.95 4.00
7i	1,3-Diethyl-2-(2,4,6-triphenylphenyl)-1*H*-benzimidazolium	35	303-304	$C_{35}H_{31}ClN_2O_4$ (579.1)	72.59 72.65	5.40 5.50	4.84 4.95
8a	3-Methyl-2-(2,4,6-triphenylphenyl)-benzothiazolium	44	324-325	$C_{32}H_{24}ClNO_4S$ (554.1)	69.37 69.41	4.37 4.40	2.53 2.62
8b	3-Methyl-2-[4-(4-methylphenyl)-2,6-diphenylphenyl]benzothiazolium	37	316-317	$C_{33}H_{26}ClNO_4S$ (568.1)	69.77 69.90	4.61 4.80	2.47 2.53
8c	2-[4-(4-Methoxyphenyl)-2,6-diphenylphenyl]-3-methylbenzothiazolium	41	292-293	$C_{33}H_{26}ClNO_5S$ (584.1)	67.86 67.95	4.49 4.59	2.40 2.37
8d	2-[4-(4-Chlorophenyl)-2,6-diphenylphenyl]-3-methylbenzothiazolium	36	304-305	$C_{32}H_{23}Cl_2NO_4S$ (588.5)	65.31 65.40	3.94 4.05	2.38 2.39
8e	2-[4-(4-Bromophenyl)-2,6-diphenylphenyl]-3-methylbenzothiazolium	50	314-315	$C_{32}H_{23}BrClNO_4S$ (633.0)	60.72 60.80	3.66 3.75	2.21 2.22
8f	3-Methyl-2-[2,6-bis(4-methylphenyl)-4-phenylphenyl]benzothiazolium	48	322-323	$C_{34}H_{28}ClNO_4S$ (582.1)	70.15 70.30	4.85 4.90	2.41 2.50
8g	2-[2,6-Bis(4-chlorophenyl)-4-phenylphenyl]-3-methylbenzothiazolium	50	328-329	$C_{32}H_{22}Cl_3NO_4S$ (623.0)	61.70 61.80	3.56 3.62	2.25 2.30
8h	2-[2,6-Bis(4-bromophenyl)-4-phenylphenyl]-3-methylbenzothiazolium	65	329-331	$C_{32}H_{22}Br_2ClNO_4S$ (711.9)	53.99 54.01	3.11 3.23	1.97 2.15
8i	3-Ethyl-2-(2,4,6-triphenylphenyl)benzothiazolium	34	282-283	$C_{33}H_{26}ClNO_4S$ (568.1)	69.77 69.52	4.61 4.69	2.47 2.40

anhydrobases [8,9], which attack the cations of the salts **1/9** with the nucleophilic β-carbon atom in the preferred position 2 [2,3,11]. Then *via* ring opening/ring closure, a new benzene ring is built up containing five carbon atoms of the pyrylium/thiopyrylium system and one C-atom of the nucleophile, which connects the former positions 2 and 6 of the pyrylium and thiopyrylium ring, respectively (2,6-[C_5+C] transformation [12]). By comparison with the transformation **1** + **2** → **3** (2,5-[C_4+C_2] reaction [6]) it becomes evident that the structural features of the benzene anellated five-membered heterocycle have a considerable influence on the type of ring transformation occurred and hence on the kind of products isolated.

The results of the elemental analyses and the spectroscopic data (*cf.* Tables 1 and 2) strongly support the structure proposed for the 1*H*-benzimidazolium and benzothiazolium salts **7/8**. In the ^{1}H nmr spectra the *N*-bonded methyl groups give the expected singuletts (**7a-h**: 3.50-3.58 ppm, **8a-h**: 3.78-3.86 ppm). The aromatic protons of the aryl rings and the benzene system condensed to the five-membered heterocycles resonate at 7.02-8.39 ppm; in this region a singulett at 7.94-8.07 ppm is observed which can be assigned to the protons in 3- and 5-position of the 2,4,6-triarylphenyl substituent. The FAB mass spectra, recorded for the compounds **7a,b** and **8a,b**, show the mass peaks of the corresponding 1*H*-benzimidazolium and benzothiazolium cations. A characteristic feature of the uv spectra is a strong absorption at 245-260 nm together with a band of lower intensity at higher wavelengths (**7a-i**: 289-305 nm, **8a-i**: 323-344 nm). The results of the elemental analyses and the characteristic perchlorate ir absorption [13] at 1076-1094 cm^{-1} indicate that the transformation products were isolated as perchlorate salts.

Table 2
Spectral Data for the 2-(2,4,6-Triarylphenyl)-1*H*-benzimidazolium Perchlorates **7** and for the 2-(2,4,6-Triarylphenyl)benzothiazolium Perchlorates **8**

Compound	IR (KBr) (cm^{-1}) ClO_4	UV (CH_3CN) λ_{max}(nm) (log ε)	^{1}H-NMR (DMSO-d_6) [a] δ (ppm)
7a [b]	1090	252 (4.64), 291 (4.48)	3.51 (s, 6H, NCH_3), 7.21-7.99 (m, 19H, arom-H), 8.05 (s, 2H, 3-, 5-H)
7b [b]	1092	255 (4.58), 296 (4.51)	2.33 (s, 3H, CH_3), 3.51 (s, 6H, NCH_3), 7.21-7.89 (m, 18H, arom-H), 8.01 (s, 2H, 3-, 5-H)
7c	1091	231 sh (4.54), 259 (4.50), 305 (4.51)	3.50 (s, 6H, NCH_3), 3.78 (s, 3H, OCH_3), 7.04-7.96 (m, 18H, arom-H), 8.00 (s, 2H, 3-, 5-H)
7d	1092	254 (4.61), 292 (4.51)	3.52 (s, 6H, NCH_3), 7.22-8.05 (m, 18H, arom-H), 8.06 (s, 2H, 3-, 5-H)
7e	1090	256 (4.63), 292 (4.55)	3.52 (s, 6H, NCH_3), 7.21-7.97 (m, 18H, arom-H), 8.05 (s, 2H, 3-, 5-H)
7f	1094	258 (4.65), 293 (4.39)	2.16 (s, 6H, CH_3), 3.52 (s, 6H, NCH_3), 7.02-7.91 (m, 17H, arom-H), 7.96 (s, 2H, 3-, 5-H)
7g	1089	258 (4.70), 292 (4.46)	3.58 (s, 6H, NCH_3), 7.23-7.96 (m, 17H, arom-H), 8.06 (s, 2H, 3-, 5-H)
7h	1093	260 (4.71), 292 (4.44)	3.59 (s, 6H, NCH_3), 7.17-7.99 (m, 17H, arom-H), 8.05 (s, 2H, 3-, 5-H)
7i	1076	252 (4.65), 289 (4.45)	0.88 (t, 6H, CH_3), 4.11 (q, 4H, NCH_2), 7.18-8.00 (m, 19H, arom-H), 8.07 (s, 2H, 3-, 5-H)
8a [b]	1091	246 (4.63), 325 (4.21)	3.80 (s, 3H, NCH_3), 7.26-8.35 (m, 19H, arom-H), 7.98 (s, 2H, 3-, 5-H)
8b [b]	1093	246 (4.60), 332 (4.24)	2.02 (s, 3H, CH_3), 3.78 (s, 3H, NCH_3), 7.29-8.34 (m, 18H, arom-H), 7.96 (s, 2H, 3-, 5-H)
8c	1092	245 (4.59), 279 sh (4.37), 344 (4.26)	3.78 (s, 3H, OCH_3), 3.78 (s, 3H, NCH_3), 7.03-8.34 (m, 18H, arom-H), 7.94 (s, 2H, 3-, 5-H)
8d	1086	247 (4.64), 323 (4.26)	3.79 (s, 3H, NCH_3), 7.29-8.34 (m, 18H, arom-H), 8.01 (s, 2H, 3-, 5-H)
8e	1093	247 (4.62), 323 (4.27)	3.79 (s, 3H, NCH_3), 7.29-8.34 (m, 18H, arom-H), 8.01 (s, 2H, 3-, 5-H)
8f	1089	251 (4.67), 332 (4.19)	2.18 (s, 6H, CH_3), 3.80 (s, 3H, NCH_3), 7.05-8.36 (m, 17H, arom-H), 7.91 (s, 2H, 3-, 5-H)
8g	1089	249 (4.68), 325 (4.22)	3.87 (s, 3H, NCH_3), 7.35-8.39 (m, 17H, arom-H), 8.00 (s, 2H, 3-, 5-H)
8h	1085	250 (4.70), 324 (4.23)	3.88 (s, 3H, NCH_3), 7.26-8.38 (m, 17H, arom-H), 8.00 (s, 2H, 3-, 5-H)
8i	1090	246 (4.65), 328 (4.18)	0.97 (t, 3H, CH_3), 4.39 (q, 2H, NCH_2), 7.27-8.39 (m, 19H, arom-H), 7.99 (s, 2H, 3-, 5-H)

[a] 3- and 5-H denotes the protons in 3- and 5-position of the 2,4,6-triarylphenyl substituent, respectively, and arom-H the other protons bonded to the aromatic/heteroaromatic rings. [b] Mass Spectra (FAB): m/z **7a** 451 [$C_{33}H_{27}N_2^+$], **7b** 465 [$C_{34}H_{29}N_2^+$], **8a** 454 [$C_{32}H_{24}NS^+$], **8b** 468 [$C_{33}H_{26}NS^+$].

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ^{1}H nmr spectra were recorded on a Varian Gemini 200 spectrometer (199.975 MHz, DMSO-d_6, 25°, HMDSO as internal standard), ir spectra were obtained on a Perkin-Elmer FTIR 2000 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** [14], **1b** [15], **1c** [16], **1d** [17], **1e** [18], **1f-h** [19] and the thiopyrylium perchlorate **9** [10] were prepared according to literature procedures; the 1*H*-benzimidazolium and benzothiazolium salts **5/6** were synthesized by alkylation of 1-alkyl-2-methyl-1*H*-benzimidazol and 2-methylbenzothiazol, respectively, with dialkylsulfates as described in refs [20,21].

Preparation of 2-(2,4,6-Triarylphenyl) Substituted 1*H*-Benzimidazolium Perchlorates **7** from 2,4,6-Triarylpyrylium Perchlorates **1** and 2-Methyl-1*H*-benzimidazolium Salts **5**. 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-1*H*-benzimidazolium salt **5** the reaction mixture was heated under reflux for 2 hours. The 2-(2,4,6-triarylphenyl)-1*H*-benzimidazolium perchlorates formed crystallized from the hot reaction mixture. They were filtered off by suction, washed with water, ethanol and diethyl ether and purified by dissolving in a minimal amount of hot acetonitrile and subsequent precipitation with diethyl ether.

Preparation of 2-(2,4,6-Triarylphenyl) Substituted Benzothiazolium Perchlorates **8** from 2,4,6-Triarylpyrylium Perchlorates **1** and 2-Methylbenzothiazolium Salts **6**. General Procedure (*cf.* Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles of pyrylium perchlorate **1**, 5 mmoles of 2-methylbenzothiazolium salt **6** 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)benzothiazolium perchlorates **8** separated as crystalline solids. They were isolated and purified as described for the 1*H*-benzimidazol derivatives **7**.

Synthesis of the 2-(2,4,6-triphenylphenyl) Substituted 1*H*-Benzimidazolium and Benzothiazolium Perchlorates **7a/8a** from 2,4,6-Triphenylthiopyrylium Perchlorate (**9**) and the Methyl Derivatives **5a/6a.**

According to the general procedures for the transformation of the pyrylium salts **1** 2,4,6-triphenylthiopyrylium perchlorate (**9**) (2.12 g, 5 mmoles) was reacted with 1,2,3-trimethyl-1*H*-benzimidazolium methosulfate (**5a**) and 2,3-dimethylbenzothiazolium methosulfate (**6a**), respectively. The products were isolated and purified as described there, yields: **7a** 43%; **8a** 45%; the compounds were identical in all respects with those ones obtained from **1a** and **5a/6a**.

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