On the Formation and Reactivity of 2-Alkylidene-benzopyrans and Their 2-Amino-5,6-benzo-2H-pyran Precursors

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Abstract. A series of 2-amino-substituted 5,6-benzo-2H-pyrans **14**, 2-alkylidene-5,6-benzo-2H-pyrans **15**, and their dimers **17** are obtained, depending on the condition used, by the reaction of 2-hydroxy-benzaldehydes **1** with enamines **9** derived of (cyclo)aliphatic ketones. Compounds **14**, **15**, and **17** can be transformed into 2-alkyl-benzopyrylium salts **16** or 2-[1-(2-hydroxyphenyl)-alken-2-yl]-benzopyrylium salts **23** by treatment with mineral acids. With aromatic aldehydes or the Vilsmeier reagent the compounds **14**, **15**, or **17** are transformed into deeply colored 2-(aryl-alkenyl)-benzopyrylium perchlorates **25** or 2-(2-dialkylamino)-alkenyl-benzopyrylium salts **26**, respectively.
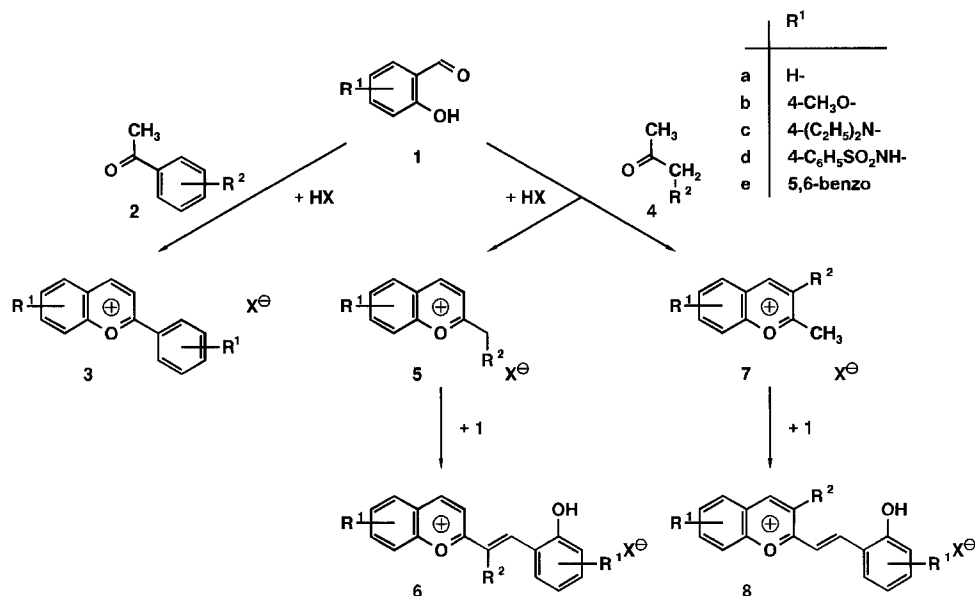
Condensation of 2-hydroxybenzaldehydes **1** with methyl ketones, in presence of a strong mineralic acid, is one of the most versatile methods for preparing benzopyrylium salts [1]. Thus, 2-aryl-benzopyrylium salts **3** can be obtained from aryl methyl ketones **2** in satisfactory yields by this route. These salts have received a lot of interest due to their deep colour, which ranges from a pale yellow to a deep blue depending upon their substitution pattern, *e.g.*, they represent the chromophoric part of the natural anthocyanins, the colored pigments of many flowers, fruits and leaves [2], and can be used, therefore, as drug colorants [3]. Several 2-aryl-benzopyrylium salts **3** have been recently claimed as spectral sensitizers for electrophotographic recording materials [4] and, so far as they exhibit an intense fluorescence, as laser or sensor dyes [5, 6].

In contrast to the 2-aryl-benzopyrylium salts **3**, the preparation of 2-alkyl-benzopyrylium salts **5** by an analogous condensation of 2-hydroxy-benzaldehydes **1** with alkyl methyl ketones **4** is problematic. Instead of 2-alkyl-benzopyrylium salts **5** the formation of 2-(2-hydroxy-phenyl-ethenyl)-benzopyrylium salts **6** usually occurs [7]. The formation of these salts **6** is assumed to proceed *via* the intermediate 2-alkyl-benzopyrylium salts **5** which react with certain electrophilic reagents such as aromatic aldehydes [8] due to their high reactivity at their 2-alkyl group; *i.e. via* the reaction of the corre-sponding methylene compounds with the starting 2-hydroxy-benzaldehyde **1**. Moreover, isomeric 2-methyl-3-alkyl-benzopyrylium salts **7** and their derived 2-(2-hydroxyphenyl-ethenyl)-benzopyrylium salts **8** can be observed in this condensation, when higher alkyl methyl ketones **4** (or unsymmetrically substituted dialkyl ketones) are used as educts [1] (Scheme 1).

Therefore, only a small number of pure 2-alkyl-benzopyrylium salts **5** have been prepared, albeit in only mentionable yields, by starting from 2-hydroxy-benzaldehydes **1** and aliphatic ketones **4**. The failure of other simple methods, when applied to the preparation of 2-alkyl-substituted benzopyrylium salts **5** has led to there being only a few previously known examples of these compounds [1]. However, their similarity to the non-benzocondensed 2-alkyl-pyrylium salts which are well documented as versatile educts for preparing deeply colored methine dyes applied in several fields of science and technology [9], stimulates the elaboration of a simple method for their preparation (or the preparation of their corresponding methylene bases as the reactive species for the formation of such dyes).

Our inital attempts at elaborating a simple route to 2-alkyl-benzopyrylium salts, which would avoid the complications of the previous mentioned methods, started from 2,4-bis-heterofunctionalized 2-alkyl-3,4-dihydro-5,6-benzo-2H-pyrans. Such compounds, *e.g.* the 2-
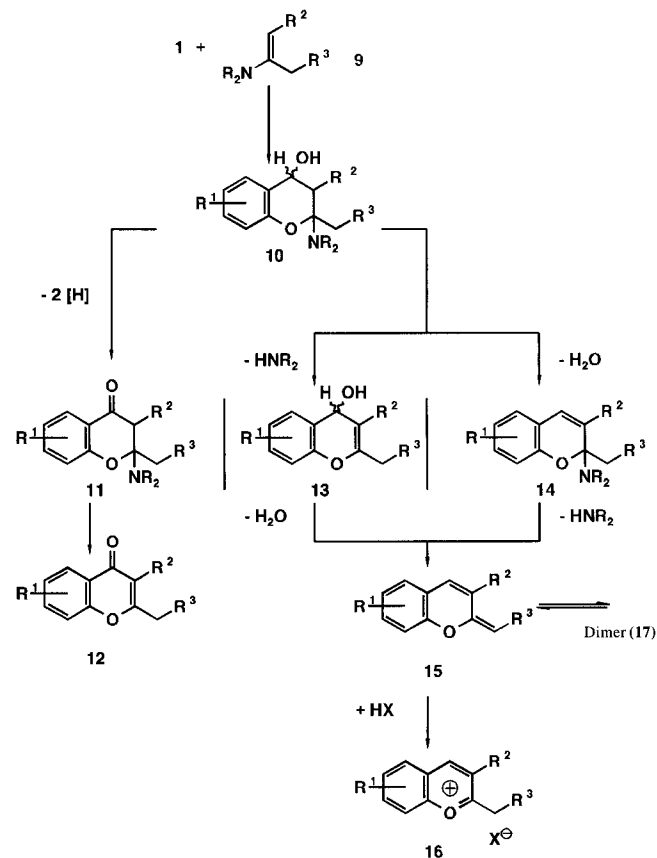
Scheme 1

dialkylamino-4-hydroxy-5,6-benzopyrans **10**, are available by the condensation of enamines **9** (derived from aliphatic ketones) with 2-hydroxy-benzaldehydes **1** [10], and should be easily converted into the corresponding 2-alkyl-substituted benzopyrylium salts **16** by their reaction with a strong mineralic acid (tandem dehydration-deamination). Surprisingly, such an elimination giving rise to the formation of 2-alkyl-benzopyrylium salts **16** is not, as yet, described in the literature. The only known transformation of the 2-dialkylamino-4-hydroxy-5,6-benzopyran educts **10**, are into corresponding 2,3-benzo-pyran-4-ones **12**, by their reaction with chromous acid in pyridine [11]; or into 2-alkylidene-5,6-benzo-pyrans **15**, by heating them at elevated temperatures [10] (*via* compounds **11**, **13**, or **14** which should be the reaction intermediates) (Scheme 2).

A series of differently substituted 2-hydroxy-benzaldehydes **1** have been condensed with the enamines **9** of several aliphatic ketones *via* the literature preparation of 2-dialkylamino-4-hydroxy-5,6-benzopyrans **10** [10]. Enamines derived from cyclic ketones were used for the most part, in order to avoid the formation of isomeric condensation products. With the exception of certain aromatic aldehydes [12] this condensation has been performed by the addition of a stoichiometric amount of 2-hydroxy-benzaldehyde **1** to a refluxing solution of the appropriate enamine **9** in toluene. Under these conditions not only the condensation of the educts **1** and **9** to the corresponding 2-dialkylamino-4-hydroxy-5,6-benzopyrans **10** occurs, but also their subsequent dehydration to give the corresponding 2-dialkyl-amino-5,6-benzo-2*H*-pyrans **14**.

These 2-dialkylamino-5,6-benzo-2*H*-pyrans **14** are usually viscous oils which exhibit a low tendency to crystallize, as are their 2-dialkylamino-4-hydroxy-5,6-benzopyran precursors **10**. However, in few examples

Scheme 2

the 2-dialkylamino-5,6-benzo-2*H*-pyrans **14** could be obtained as crystalline compounds. In this case, their identity was unambiguously assigned, as exemplified for compound **14g** (see experimetal part), by means of their elemental analysis and NMR spectra.

Surprisingly, the reaction of the 2,3-dialkyl-2-dialkyl-amino-5,6-benzo-2*H*-pyrans **14** with a strong mineralic acid, (*e.g.*, with aqueous perchloric acid), does not give, in all examples studied, the expected 2,3-dialkyl-sub-stituted benzopyrylium perchlorates **16** in any mention-able yield. Instead of these salts **16** several other products, especially the corresponding 2-(2-hydroxyphenyl-ethenyl)-benzopyrylium salts **23**, could be obtained. However, corresponding 2,3-dialkyl-benzopyrylium perchlorates **16** could be obtained, (as seen from Tab. 1), in only mentionable yields from benzopyran educts **14** by using anhydrous perchloric acid.

dride to a toluene solution of a 2-dialkylamino-5,6-ben-zo-2*H*-pyran **14**, and subsequently pouring the result-ing mixture, (after some standing at room temperature), into an excess of anhydrous ethanol. By this procedure, the 2-alkylidene-5,6-benzopyran **15** crystallized and could be isolated directly by filtration. At first glance, it seems that the 2-alkylidene-5,6-benzopyrans **15** pre-pared by this method have been obtained in mostly sat-isfactory yields. Their analytical data which are com-piled in the Tab. 2 and 3 revealed, however, that the products so obtained are mixtures of monomeric, dimer-ic, and oligomeric compounds, their relative propor-tions depend on the structure of the educts as well as on the preparation conditions used (see Tab. 2). Thus, mon-omeric 2-alkylidene-5,6-benzopyrans **15** could be de-tected in the resulting reaction mixtures in some spe-cial cases only. They could be identified by their

Tab. 1 Results of the Reaction of the Benzopyrans **14**, **15**, or **17** with Perchloric Acid

Entry	Substitution pattern R¹	R²	R³	Educt 14 Product [a]	Yield (%)	Educt 15 or Educt 17 Product [b]	Yield (%)	Product [a]	Yield (%)
a	7-(C₂H₅)₂N	-(CH₂)₂-		**16a**	60	**23a**	40	**16a**	95
b	7-(C₂H₅)₂N	-(CH₂)₃-		**16b**	40	**23b**	32	**16b**	90
c	7-(C₂H₅)₂N	-(CH₂)₄-		**16c**	50	**16c**	80	**16c**	95
d	7-CH₃O	-(CH₂)₂-		**16d**	40	**23d**	45	**16d**	90
e	7-CH₃O	-(CH₂)₃-		**16e**	40	**23e**	20	**16e**	90
f	7-CH₃O	-(CH₂)₄-		**16f**	45	**16f**	20	**16f**	80
g	5,6-(CH=CH)₂	-(CH₂)₂-		**16g**	60	**23g**	25	**16g**	95
h	5,6-(CH=CH)₂	-(CH₂)₃-		**16h**	55	**16h**	20	**16h**	95
i	5,6-(CH=CH)₂	-(CH₂)₄-		**16i**	60	**16i**	80	**16i**	95
k	7-C₆H₅SO₂NH	-(CH₂)₃-		**16k**	60	**16k**	35	**16k**	95
l	H	-(CH₂)₂-		**16l**	35	**23l**	25	**16l**	80
m	H	-(CH₂)₃-		**16m**	30	**16m**	20	**16m**	85
n	H	-(CH₂)₄-		**16n**	35	**16n**	80	**16n**	90
o	H	CH(CH₃)₂	H	**16o**	30	**16o**	80	**16o**	85
p	H	CH₃	CH₃	**16p**	30	**16p**	70	**16p**	80

[a]) Method A: using perchloric acid in acetic anhydride/ether as reagent
[b]) Method B: using aqueous perchloric acid as reagent

Therefore, a modified route for transforming the ben-zopyran intermediates **14** into the corresponding 2-al-kyl-benzopyrylium perchlorates **16** has been developed. It consist in the initial transformation of the 2-dialkyl-amino-5,6-benzo-2*H*-pyrans **14** into the 2-alkylidene-5,6-benzo-pyrans **15** by elimination of their amine moi-ety and subsequent reaction with perchloric acid to yield the required benzopyrylium perchlorates **16**. Prepara-tion of 2-alkylidene-5,6-benzopyrans **15** by heating the 2-hydroxy-benzaldehyde/enamine adducts **10** at elevat-ed temperature has been described by Kabbe *et al.* [10], but the required products can be obtained in special cases only.

The transformation of the 2-dialkylamino-5,6-benzo-2*H*-pyrans **14** into the 2-alkylidene-5,6-benzo-pyrans **15** was performed simply by the addition of acetic anhy-

¹H NMR signals at about 5.00 and 6.00 ppm which can be unambiguously attributed to the protons at their alkylene groups and at their C-4 positions, respective-ly.

The further compounds which could be detected as reaction products of the 2-alkylidene-5,6-benzopyrans **15** with acetic anhydride are dimeric 2-alkylidene-5,6-benzopyrans **17** or higher oligomers. The dimeric 2-alkylidene-5,6-benzopyrans **17** are formed mainly by starting from 2-dialkylamino-5,6-benzo-2*H*-pyran educts **14** derived from cyclopentanone and cyclohex-anone enamines. They have been unambiguously de-tected by means of mass spectroscopy and ¹H NMR, *e.g.*, they exhibit characteristic ¹H NMR signals at about 2.5 and 4.0 ppm, which can be attributed to the H at-oms linked at the C-2 alkyl groups and at C-4 posi-

Tab. 2 Characteristical Data of the 2-Alkylidene-5,6-benzo-2*H*-pyrans **15** and their Dimers **17** (for the substituent pattern see tab. 1).

Entry	Y (%)	F (°C)	Y (%)[a]	MS (*m/z*) (%)	Formula (m.w.)	C (calcd./found)	H	N
15a	85	212 – 214	10	241 (20)	$C_{16}H_{19}NO$	79.63	7.94	5.80
17a			85	482 (5)	(241.33)	78.33	7.93	6.12
15b	80	143 – 147	5	255 (100)	$C_{17}H_{21}NO$	79.96	8.29	5.49
17b			90	510 (28)	(255.36)	80.93	8.83	5.81
15c	65	253 – 255	[b]	269 (100)	$C_{18}H_{23}NO$	80.26	8.61	5.20
17c			[b]	538 (20)	(269.39)	79.94	8.93	4.89
15d	78	170 – 172	[b]	200 (87)	$C_{13}H_{12}O$	77.98	6.04	
17d			[b]	400 (42)	(200.24)	77.52	6.86	
15e	80	137 – 141	5	214 (20)	$C_{14}H_{14}O$	78.48	6.59	
17e			90	428 (7)	(214.26)	78.27	7.03	
15f	65	150 – 153	[b]	228 (90)	$C_{15}H_{16}O$	78.92	7.06	
17f			[b]	456 (16)	(228.29)	78.14	7.55	
15g	83	220 dec.	5	220 (83)	$C_{16}H_{12}O$	87.25	5.49	
17g			90	440 10)	(220.27)	86.89	6.18	
15h	85	178 – 180	[b]	234 (65)	$C_{17}H_{14}O$	87.15	6.02	
17h			[b]	468 (22)	(234.30)	86.81	6.50	
15i	63	188 – 191	[b]	248 (40)	$C_{20}H_{16}O$	87.06	6.49	
17i			[b]	496 (5)	(248.32)	86.41	6.45	
15k	78	200 dec.	[b]	339 (20)	$C_{19}H_{17}NO_3S$	67.24	5.05	4.13
17k			[b]	678 (5)	(339.41)	66.99	5.78	4.69
15l	74	160 – 165	[b]	170 (53)	$C_{12}H_{10}O$	84.68	5.92	
17l			[b]	340 (44)	(170.21)	83.47	6.17	
15m	80	173 – 176	5	184 (100)	$C_{13}H_{12}O$	84.75	6.57	
17m			90	368 (40)	(184.24)	84.61	7.27	
15n	68	117 – 120	[b]	198 (100)	$C_{14}H_{14}O$	84.81	7.12	
17n			[b]	396 (38)	(198.26)	85.08	7.81	
15o	48	135 – 139	[b]	186 (55)	$C_{13}H_{14}O$	83.83	7.58	
17o			[b]	372 (35) [c]	(186.25)	84.65	8.46	
15p	35	169 – 171	<2	172 (95)	$C_{12}H_{12}O$	83.69	7.02	
17p			70	344 (10)	(172.23)	83.96	6.89	

[a] yield of products approximately estimated by integration of their characteristical ^{1}H NMR signals (the differences to 100% corresponds to the yield of oligomers)   [b] yield could not be estimated   c) *m/z* (%) of trimer: 558 (25)

Tab. 3 ^{1}H NMR Data of the 2-Alkylidene-5,6-benzo-2*H*-pyrans **15** and their Dimers **17**

| Entry	δ values, in ppm, in $CDCl_3$ (assignment)
15a	4.68 (t, 1H, CH), 5.86 (s, 1H, CH)
17a	1.13 (t, 6H, CH_3),1.55 (m, 2H) CH_2), 2.53 (m, 1H, CH), 2.60 (t, 2H, CH_2), 3.28 (q, 4H, NCH_2), 3.95 (d, 1H, CH), 6.18 (s, 1H, CH_{aryl}), 6.30 (d, 1H, CH_{aryl}), 6.41 (d, 1H, CH_{aryl})
15b	4.77 (t, 1H, CH), 5.92 (s, 1H, CH)
17b	1.13 (t, 6H, CH_3), 1.60 (m, 4H, CH_2), 2.32 (t, 2H, CH_2), 2.60 (m, 1H, CH), 3.30 (q, 4H, NCH_2), 4.00 (m, 1H, CH), 6.16 (s, 1H, CH_{aryl}), 6.25 (d, 1H, CH_{aryl}), 6.30 (d, 1H, CH_{aryl})
15e	4.80 (t, 1H, CH), 5.98 (s, 1H, CH)
17e	1.55 (m, 4H, CH_2), 2.47 (t, 2H, CH_2), 2.60 (m, 1H, CH), 3.75 (s, 3H, OCH_3), 4.02 (m, 1H,CH), 6.41 (s, 1H, CH_{aryl}), 6.50 (d, 1H, CH), 6.58 (d, 1H, CH_{aryl})
15g [a]	5.25 (t, 1H, CH), 6.40 (s, 1H, CH)
17g	1.95 (m, 2H, CH_2), 2.70 (t, 2H, CH_2), 2.8 (m, 1H, CH), 4.2 (m, 1H, CH), 7.2–7.8 (m, 6H, CH_{aryl}),
15m	4.87 (t, 1H, CH_{aryl}), 6.01 (s, 1H, CH_{aryl})
17m	1.70 (m, 4H, CH_2), 2.22 (m, 1H, CH), 2.45 (t, 2H, CH_2), 4.04 (m, 1H, CH), 6.8–7.2 (m, 4H, CH_{aryl})
17p [a]	0.89 (s, 6H, CH_3), 1.26 (s, 3H, CH_3), 2.60 (m, 1H, CH), 3.40 (m, 1H, CH), 6.70 (m, 4H, CH_{aryl})

[a] measured in toluene -d_8

tions, respectively. In all other cases oligomeric products seem to be the main products of the reaction mixtures obtained after the addition of acetic anhydride to the corresponding 2-dialkylamino-5,6-benzo-2*H*-pyrans **14**.

The actual structure of the dimeric 2-alkylidene-5,6-benzopyrans **17** is assumed to be cyclic, and its geometry has been optimized by means of a force-field calculation using standard programme.

It is worth mentioning that the dimeric 2-alkylidene-5,6-benzopyran **17m** obtained from 2-hydroxy-benzaldehyde **1a** (R^1 = H) and pyrrolidino-cyclohexene **9** (R_2N
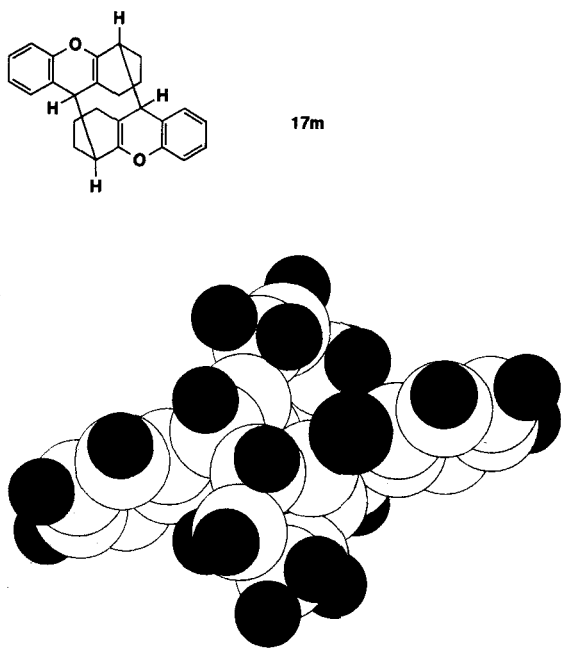
Fig. 1 Optimized molecular structure of the cyclic dimer **17m** of the α,3-trimethylene-bridged 2-ethylidene-5,6-benzopyran **15m**

= pyrrolidino, R^2, R^3 = -(CH$_2$)$_2$-) has the same melting point than the 2-alkylidene-5,6-benzopyran **15l** described by Kabbe et al. [10] who, however, gave no exact proofs for the structure of his prepared product. Due to this unlikely coincidence the structure given by Kabbe as a monomeric 2-alkylidene-5,6-benzopyran **15** may have to be revised.

Destillation of the dimeric 2-alkylidene-5,6-benzopyrans **17** in some cases gives their monomeric forms **15**. However, after a short-time standing (few days) at room temperature these monomers **15** readily re-dimerize **17**.

The reaction of the 2-alkylidene-5,6-benzopyrans **15** or their dimers **17** with mineralic acid gives a rather curious result. In contrats to the expected reaction, this does not give the desired 2-alkyl-substituted benzopyrylium salts **16** in a straightforward way. Rather, by addition of aqueous perchloric acid to a solution of 2-alkylidene-5,6-benzopyran **15** or its dimer **17** in a polar solvent, such as acetonitrile, a deeply colored solution has been obtained in many cases. From this solution a crystalline compound precipitates immediately after the acid addition. These are surprisingly identified as the corresponding 2-(2-hydroxyaryl-2-alkenyl)-benzopyrylium salts **23** (see Tab. 1), which were previously mentioned and available either by the reaction of the above-mentioned 2-dialkylamino-5,6-benzo-2H-pyrans **14** with aqueous perchloric acid or by the condensation

of two equivalent of a 2-hydroxy-benzaldehyde **1** with one equivalent of an aliphatic ketone **4** in the presence of a mineralic acid [7]. Therefore, only such salts **23** which were as yet unknown are described and characterised in the experimental section.

The formation of 2-(2-hydroxyarylalkenyl)-benzopyrylium salts **23** from the 2-alkylidene-5,6-benzopyrans **15** or their dimers **17** is surprisingly in so far as the starting compounds do not contain any free 2-hydroxy-benzaldehyde **1**, which seems to be the necessary precursor. For explaining the formation of these 2-(2-hydroxyarylalkenyl)-benzopyrylium salts **23** in the course of the protonation of educts **15** or **17** it is to assume that the reaction proceeds via the steps depicted in Scheme 3.
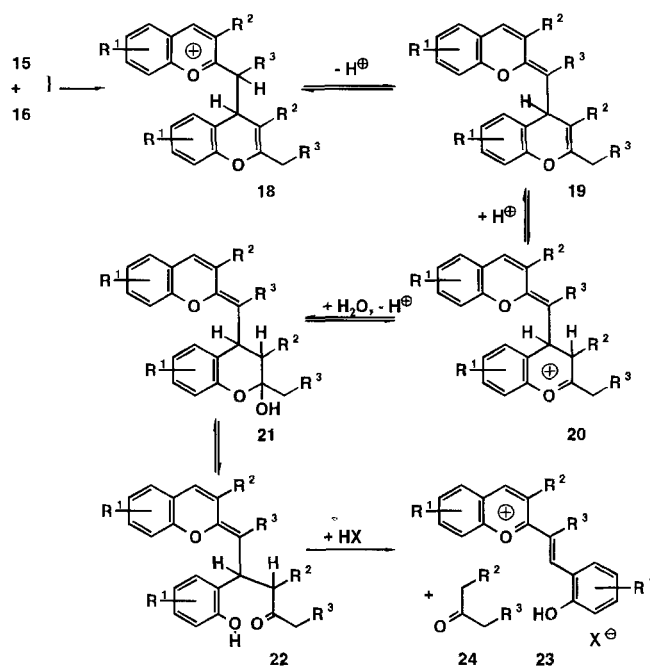
Scheme 3

According to this scheme the 2-(2-hydroxyarylalkenyl)-benzopyrylium salts **23** result from the reaction of the starting 2-alkylidene-5,6-benzopyrans **15** with the formed 2-alkyl-benzopyrylium salts **16** by their initial protonation to give rise to the formation of species **18**, which are subsequently transformed by several consecutive steps into the products **23**. Essential steps in this reaction sequence are i) the addition of a nucleophile HY, such as water (Y= OH), to intermediates **20**, to give the adducts **21**, which are transformed under ring-opening, into the intermediates **22**; and ii) a retro-Michael addition which transforms intermediates **22** into a mixture of the products **23** and the ketonic component **24** of the enamines used as educts for the preparation of the benzopyrylium salts **16** or their precursors.

The ketones **24** were identified in the filtrated reaction mixtures as their 2,4-dinitrophenylhydrazones.

An argument for confirmation of this postulated reaction scheme is our finding that the 2-alkyl-benzopyrylium salts **16** could be obtained, in all examined cases, in satisfactory yields if the addition of acids to the 2-alkylidene-5,6-benzopyrans **15** or their dimers **17** is performed under strictly anhydrous conditions (see Tab. 1, Method A).

In Tab. 1 the results obtained by addition of perchloric acid to a solution of the 2-alkylidene-5,6-benzopyrans **15** or their dimers **17** are summarized. By using aqueous perchloric acid (Method B), the desired 2-alkyl-benzopyrylium salt **16** have only been obtained in some special cases. Usually, the formation of corresponding 2-(2-hydroxyaryl-2-alkenyl)-benzopyrylium salts **23** or mixtures of these benzopyrylium salts **23** with the non-condensed 2-alkyl-benzopyrylium salts **16** occurs.

In Tab. 4 and 5 the analytical data of the prepared 2-alkyl-benzopyrylium salt **16** are summarised.

Although a series of known and unknown 2-alkyl-benzopyrylium salts **16** have been prepared, in a simple manner, from their 2-dialkylamino-5,6-benzo-2H-pyrans **14** or 2-alkylidene-5,6-benzopyrans **15**, these salts **16**

seem not to be versatile intermediates for further transformations due to the complications occuring in the course of their preparation. Instead, the 2-alkylidene-5,6-benzopyrans **15** or their dimers **17** as well as their precursors **14** are much more better starting materials, *e.g*, for the synthesis of methine dyes containing the benzopyrylium moiety. Thus, deeply colored styryl dyes **25** could be prepared by heating an equimolar mixture of an aromatic aldehyde and a 2-alkylidene-5,6-benzo-2H-pyran **15** in acetic anhydride containing some magnesium perchlorate. The benzopyrylium derived styryl dyes **25** so formed, crystallise after cooling from the reaction mixtures, and can be isolated directly by filtration.

Furthermore, the reaction of 2-dialkylamino-substituted 5,6-benzo-2H-pyrans **14** with the Vilsmeier reagent (prepared as usual from dimethylformamide and $POCl_3$) gives 2-dimethylaminoalkenyl-substituted benzopyrylium salts **26**. These salts have been isolated advantageously as perchlorates by addition of perchloric acid to the reaction mixture after it has been dilutied with methanol.

The 2-(aryl-alkenyl)-benzopyrylium perchlorates **25** and 2-dimethylaminoalkenyl-substituted benzopyrylium perchlorates **26** so prepared are summarized in Tab. 6 and 7, respectively.

Tab. 4 Benzopyrylium Perchlorates **16**

Entry	F (°C)	λ_{max}[a])	Formula (m.w.)	C (calcd./found)	H	N
16a	174 – 177	495	$C_{16}H_{20}ClNO_5$	56.17	5.85	4.10
			(341.79)	56.08	6.15	3.96
16b	173 – 175	485	$C_{17}H_{22}ClNO_5$	57.39	6.33	3.94
			(355.79)	56.42	6.58	3.72
16c	167 (167 [13])	485				
16d	181 – 183	396	$C_{13}H_{13}ClO_6$	51.88	4.32	–
			(300.69)	51.74	4.73	–
16e	148 – 150	392	$C_{14}H_{15}ClO_6$	53.38	4.77	–
			(314.72)	53.28	4.93	–
16f	167 – 170	390	$C_{15}H_{17}ClO_6$	54.75	5.17	–
			(328.74)	54.77	5.43	
16g	217 – 220 (218 – 220 [14])	415 (417 [14])				
16h	218 – 222 (218 – 222 [14])	411 (413 [14])				
16i	209 – 211 (209 – 211 [14])	407 (410 [14])				
16l	202 – 205	354	$C_{12}H_{11}ClO_5$	53.20	4.06	–
			(270.66)	53.12	4.42	–
16m	198 – 200 (198 – 200 [13])	341				
16n	180 – 182	339	$C_{14}H_{15}ClO_5$	56.24	5.02	–
			(298.72)	56.18	5.34	–
16o	175 – 178	334	$C_{13}H_{15}ClO_5$	54.41	5.23	–
			(286.71)	54.32	5.57	–
16p	183 – 186	336	$C_{12}H_{13}ClO_5$	52.81	4.77	–
			(272.68)	52.73	4.97	

[a]) Due to the instability of the compounds **16** in solution their absorption data have been estimated qualitatively only.
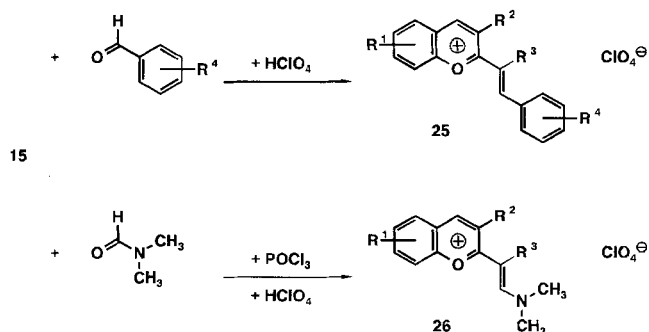
Scheme 4

Tab. 5 Characteristic ^{1}H NMR Data of Benzopyrylium Perchlorates **16**

Entry	^{1}H NMR, δ values, in ppm, measured in DMSO-d_6 (assignment)
16a	1.26 (t, 6H, CH$_3$), 1.95 (m, 2H, CH$_2$), 2.93 (t, 2H, CH$_2$), 3.12 (t, 2H, CH$_2$) 3.66 (q, 4H, CH$_2$), 7.12 (s, 1H, CH$_{aryl}$), 7.37 (d, 1H, CH$_{aryl}$), 7.82 (d, 1H, CH$_{aryl}$), 8.34 (s, 1H, CH$_{aryl}$)
16b	1.22 (t, 6H, CH$_3$), 1.92 (m, 4H, CH$_2$), 2.75 (t, 2H, CH$_2$), 3.02 (t, 2H, CH$_2$) 3.68 (q, 4H, NCH$_2$), 7.10 (s, 1H, CH$_{aryl}$), 7.52 (d, 1H, CH$_{aryl}$), 7.94 (d, 1H, CH$_{aryl}$), 8.62 (s, 1H, CH$_{aryl}$)
16c [a)	1.34 (t, 6H, CH$_3$), 1.77 (m, 2H, CH$_2$), 1.88 (m, 2H, CH$_2$), 1.94 (m, 2H, CH$_2$), 2.96 (t, 2H, CH$_2$), 3.27 (t, 2H, CH$_2$), 3.74 (q, 4H, NCH$_2$), 7.01 (d, 1H, CH$_{aryl}$), 7.44 (dd, 1H, CH$_{aryl}$), 7.88 (d, 1H, CH$_{aryl}$), 8.44 (s, 1H, CH$_{aryl}$)
16l	2.08 (m, 4H, CH$_2$), 3.21 (t, 2H, CH$_2$), 3.52 (t, 2H, CH$_2$), 8.01 (m, 1H, CH) 8.30 (m, 3H, CH$_{aryl}$), 9.28 (s, 1H, CH$_{aryl}$)
16m	1.89 (m, 2H, CH$_2$), 2.05 (m, 4H, CH$_2$), 3.26 (t, 2H, CH$_2$), 3.67 (t, 2H, CH$_2$), 8.03 (m, 1H, CH$_{aryl}$), 8.29 (m, 3H, CH$_{aryl}$), 9.30 (s, 1H, CH$_{aryl}$)

[a) measured in CD$_3$NO$_2$

Both types of benzopyrylium perchlorates **25** and **26** have been unambiguously characterized by their elemental analyses and NMR spectroscopic data which are collected in the Tab. 8 – 10.

A mentionable result concerning the preparation of the 2-dimethylaminoalkenyl-substituted benzopyrylium perchlorates **26o** and **26p** from the 7-benzosulfonylamino-substituted 5,6-benzo-2H-pyran precursors **14q** (R^1 = 7-C$_6$H$_5$SO$_2$NH, R^2,R^3=(CH$_2$)$_2$) and **14k**, resp., is found in the course of the Vilsmeier reaction of these compounds. Their 7-benzosulfonamido group is replaced by a dimethyl-formamidino group, giving rise to the formation of the 7-(3-N-dimethylformamidino)-substituted 2-dimethylamino-benzopyrylium perchlorates **26o** and **26p**. Depending on the work-up conditions, both these compounds could be isolated as hydrodiperchlorates **26o·HClO$_4$** and **26p·HClO$_4$**. With weak bases, these salts can be transformed into their corresponding monoperchlorates **26o** and **26p**, respectively. It is worth mentioning that both compounds **26o** and **26p** are, as is similar to the 7-diethylamino-substituted salts **26l – 26n**, rather stable at room temperature against treatment with bases such as aqueous ammonia or aqueous alkali hydroxides. This behaviour contrasts significantly with the other 2-dimethylamino-alkenyl-benzopyrylium perchlorates **26a – 26k** which are rather sensitive to bases or nucleophiles. Obviously, the 7-diethylamino and 7-formamidino substituted 2-dimethyl-amino-alkenyl-benzopyrylium perchlorates **26l – 26p** possess, as can be derived from their NMR spectroscopic data, a polymethine-like electronic structure with a strong charge alternation along their conjugated π-system [15].

Tab. 6 2-(2-Aryl-ethenyl)-benzopyrylium Perchlorates **25**

Entry	R^1	R^2 R^3	R^4	Yield (%)	F (°C)	λ_{max} (log)
25a	H	CH$_3$ CH$_3$	H	75	167 – 170	449 (4.23)
25b	H	-(CH$_2$)$_4$-	H	75	216 – 219	469 (4.41)
25c	5,6-benzo	-(CH$_2$)$_3$-	H	82	192 – 195	523 (4.04)
25d	5,6-benzo	-(CH$_2$)$_4$-	H	80	197 – 198	422 (4.17)
25e	7-(C$_2$H$_5$)$_2$N	-(CH$_2$)$_3$-	H	85	211 – 214	565 (4.42)
25f	H	CH$_3$ CH$_3$	4-CH$_3$O	80	140 – 142	517 (4.43)
25g	H	-(CH$_2$)$_4$-	4-CH$_3$O	78	198 – 201	538 (4.37)
25h	5,6-benzo	-(CH$_2$)$_2$-	4-CH$_3$O	85	250 – 253	590 (4.83)
25i	5,6-benzo	-(CH$_2$)$_3$-	4-CH$_3$O	87	242 – 243	577 (4.46)
25j	5,6-benzo	-(CH$_2$)$_4$-	4-CH$_3$O	82	243 – 245	546 (4.56)
25k	7-(C$_2$H$_5$)$_2$N	-(CH$_2$)$_3$-	4-CH$_3$O	85	194 – 196	587 (4.31)
25l	H	H CH(CH$_3$)$_2$	4-(CH$_3$)$_2$N	70	178 – 180	643 (4.82)
25m	H	CH$_3$ CH$_3$	4-(CH$_3$)$_2$N	83	182 – 185	650 (4.71)
25n	H	-(CH$_2$)$_2$-	4-(CH$_3$)$_2$N	85	236 – 239	687 (4.67)
25o	H	-(CH$_2$)$_3$-	4-(CH$_3$)$_2$N	77	197 – 200	690 (4.99)
25p	H	-(CH$_2$)$_4$-	4-(CH$_3$)$_2$N	87	200 – 203	689 (4.81)
25q	5,6-benzo	-(CH$_2$)$_2$-	4-(CH$_3$)$_2$N	95	248 – 250	713 (4.92)
25r	5,6-benzo	-(CH$_2$)$_3$-	4-(CH$_3$)$_2$N	92	218 – 221	710 (4.83)
25s	5,6-benzo	-(CH$_2$)$_4$-	4-(CH$_3$)$_2$N	85	228 – 231	692 (4.76)
25t	7-(C$_2$H$_5$)$_2$N	-(CH$_2$)$_2$-	4-(CH$_3$)$_2$N	90	230 – 232	718 (5.01)
25u	7-(C$_2$H$_5$)$_2$N	-(CH$_2$)$_3$-	4-(CH$_3$)$_2$N	90	215 – 218	703 (4.71)
25v	7-(C$_2$H$_5$)$_2$N	-(CH$_2$)$_4$-	4-(CH$_3$)$_2$N	87	208 – 211	664 (4.76)

Tab. 7 2-(2-Dimethylamino-ethenyl)-substituted Benzopyrylium Perchlorates **26** and Diperchlorates **26 · HClO₄**

Entry	R¹	R²	R³	Y (%) (method)	F (°C)	λ_max [a]) (log ε)	λ_max [a]) (Φ)
26a	H	CH₃	H	16 (A)	207 – 209	444 (4.41)	–
26b	H	CH₃	CH₃	48 (A)	340 – 343	466 (4.33)	–
26c	H	-(CH₂)₂-		60 (A)	292 – 295	484 (4.34)	532 (40 %)
26d	H	-(CH₂)₃-		66 (A)	248 – 250	466 (4.45)	555 (7 %)
26e	H	-(CH₂)₄-		63 (A)	187 – 189	464 (4.43)	572 (4 %)
26f	5,6-benzo	-(CH₂)₂-		56 (A)	318 – 320	524 (4.46)	577 (100 %)
26g	5,6-benzo	-(CH₂)₃-		52 (A)	268 – 271	534 (4.32)	595 (49 %)
26h	5,6-benzo	-(CH₂)₄-		26 (A)	240 – 243	511 (4.45)	607 (10 %)
26i	7-OCH₃	-(CH₂)₂-		60 (A)	174 – 176	507 (4.43)	557 (100 %)
26j	7-OCH₃	-(CH₂)₃-		51 (A)	206 – 208	514 (4.31)	572 (19 %)
26k	7-OCH₃	-(CH₂)₄-		45 (A)	168 – 169	495 (4.37)	596 (4 %)
26l	7-(C₂H₅)₂N	-(CH₂)₂-		56 (B)	270 – 272	574 (4.68)	611 (100 %)
26m	7-(C₂H₅)₂N	-(CH₂)₃-		41 (B)	203 – 205	576 (4.76)	605 (100 %)
26n	7-(C₂H₅)₂N	-(CH₂)₄-		20 (B)	145 – 147	584 (4.70)	612 (49 %)
26o [b])	7-(C₂H₅)₂N–CH=N	-(CH₂)₂-		30 (C)	238 – 240 (dec.)	539 (4.47)	596 (100 %)
26p [c])	7-(C₂H₅)₂N–CH=N	-(CH₂)₃-		41 (C)	215 – 217 (dec.)	547 (4.48)	595 (100 %)

[a]) in methylene chloride   [b]) **26o·HClO₄**: _max 508 nm; no fluorescence;   [c]) **26p·HClO₄**: _max 514 nm; no fluorescence;

Tab. 8 ¹H NMR Data of 2(2-Dimethylaminoethenyl)-substituted Benzopyrylium Perchlorates **26** and Hydrodiperchlorates **26·HClO₄**

Entry	δ values in ppm, measured in DMSO-d₆ (assignment)
26a	2.22 (s, 3H, CH₃), 3.39 (s, 3H, NCH₃), 3.57 (s, 3H, NCH₃), 5.87 ((d, 1H, CH),7.40 (t, 1H, CH_aryl), 7.54 (d, 1H, CH_aryl), 7.65 (d, 1H, CH_aryl), 7.66 (t, 1H, CH_aryl), 7.79 (s, 1H, CH_aryl), 8.86 (d, 1H, CH)
26b	1.89 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 3.48 (s, 3H, NCH₃), 3.55 (s, 3H, CH₃), 7.20 (t, 1H, CH_aryl), 7.25 (s, 1H, CH_aryl), 7.27 (d, 1H, CH_aryl), 7.41 (d, 1H, CH_aryl), 7.42, d, 1H, CH_aryl), 10.14 (s, 1H, CH)
26c [a])	3.03 (t, 2H, CH₂), 3.21 (t, 2H, CH₂), 3.57 (s, 6H, NCH₃), 7.30 (s, 1H, CH_aryl), 7.35 (t, 1H, CH_aryl), 7.41 (d, 1H, CH_aryl), 7.50 (d, 1H, CH_aryl), 7.52 (t, 1H, CH_aryl), 8.28 (s, 1H, CH)
26d [a])	1.85 (q, 2H, CH₂), 2.75 (t, 2H, CH₂), 2.86 (t, 2H, CH₂), 3.60 (s, 3H, NCH₃), 3.63 (s, 3H, NCH₃), 7.31 (t, 1H, CH_aryl), 7.32 (s, 1H, CH_aryl), 7.42 (d, 1H, CH_aryl), 7.50 (d, 1H, CH_aryl), 7.54 (t, 1H, CH_aryl), 8.60 (s, 1H, CH)
26e	1.83 (q, 4H, CH₂), 2.67 (t, 2H, CH₂), 2.80 (t, 2H, CH₂), 3.45 (s, 3H, NCH₃), 3.63 (s, 3H, CH₃), 7.28 (t, 1H, CH_aryl), 7.46 (s, 1H, CH_aryl), 7.51 (d, 1H, CH_aryl), 7.52 (d, 1H, CH_aryl), 7.54 (t, 1H, CH_aryl), 8.76 (s, 1H, CH)
26f	3.06 (t, 2H, CH₂), 3.15 (t, 2H,CH₂), 3.47 (s, 3H, NCH₃), 3.53 (s, 3H, NCH₃), 7.59 (d, 1H, CH_aryl), 7.64 (t, 1H, CH_aryl), 7.74 (t, 1H, CH_aryl), 8.05 (d, 1H, CH_aryl), 8.15 (d, 1H, CH_aryl), 8.37 (s, 1H, CH_aryl), 8.38 (s, 1H, CH), 8.51 (d, 1H, CH_aryl),
26g	1.80 (q, 2H, CH₂), 2.80 (t, 2H, CH₂), 2.82 (t, 2H, CH₂), 3.51 (s, 3H, NCH₃), 3.60 (s, 3H, NCH₃), 7.63 (t, 1H, CH_aryl), 7.72 (d, 1H, CH_aryl), 7.74 (t, 1H, CH_aryl), 8.18 (d, 1H, CH_aryl), 8.43 (s, 1H, CH_aryl), 8.51 (d, 1H, CH_aryl), 8.64 (s, 1H, CH)
26h	1.89 (q, 4H, CH₂), 2.73 (t, 2H, CH₂), 2.96 (t, 2H, CH₂), 3.45 (s, 3H, NCH₃), 3.61 (s, 3H, NCH₃), 7.61 (t, 1H, CH_aryl), 7.72 (t, 1H, CH_aryl), 7.74 (d, 1H, CH_aryl), 8.02 (d, 1H, CH_aryl), 8.16 (d, 1H, CH_aryl), 8.41 (s, 1H, CH_aryl), 8.48 (d, 1H, CH_aryl), 8.73 (s, 1H, CH)
26i	2.91 (t, 2H, CH₂), 3.10 (t, 2H, CH₂), 3.46 (s, 3H, NCH₃), 3.52 (s, 3H, NCH₃), 3.85 (s, 3H, OCH₃), 6.99 (dd, 1H, CH_aryl), 7.01 (s, 1H, CH_aryl), 7.45 (s, 1H, CH_aryl), 7.54 (d, 1H, CH_aryl), 8.38 (s, 1H, CH)
26j	1.73 (q, 2H, CH₂), 2.65 (t, 2H, CH₂), 2.76 (t, 2H, CH₂), 3.50 (s, 3H, NCH₃), 3.60 (s, 3H, NCH₃), 3.86 (s, 3H, OCH₃), 6.95 (dd, 1H, CH_aryl), 7.23 (s, 1H, CH_aryl), 7.50 (s, 1H, CH_aryl), 7.52 (d, 1H, CH_aryl), 8.66 (s, 1H, CH)
26k	1.82 (q, 4H, CH₂), 2.67 (t, 2H, CH₂), 2.77 (t, 2H, CH₂), 3.43 ((s, 3H, NCH₃), 3.60 (s, 3H, NCH₃), 3.85 (s, 3H, OCH₃), 6.92 (dd, 1H, CH_aryl), 7.17, (s, 1H, CH_aryl), 7.46 (d, 1H, CH_aryl), 7.48 (s, 1H, CH_aryl), 8.69 (s, 1H, CH)
26l	1.13 (t, 6H, CH₃), 2.87 (t, 2H, CH₂), 3.07 (t, 2H, CH₂), 3.42 (q, 4H, NCH₂), 3.43 (s, 6H, NCH₃), 6.65 (s, 1H, CH_aryl), 6.77 (dd, 1H, CH_aryl), 7.38 (d, 1H, CH_aryl), 7.42 (s, 1H, CH_aryl), 8.17 (s, 1H, CH)
26m	1.14 (t, 6H, CH₃), 1.71 (q, 2H, CH₂), 2.60 (t, 2H, CH₂), 2.75 (t, 2H, CH₂), 3.44 (4H, NCH₃), 3.46 (s, 6H, NCH₃), 6.77 (dd, 1H, CH_aryl), 6.79 (s, 1H, CH_aryl), 7.38 (d, 1H, CH_aryl), 7.46 (s, 1H, CH_aryl), 8.41 (s, 1H, CH)
26n	1.14 (t, 6H, CH₃), 1.80 (q, 4H, CH₂), 2.69 (t, 2H, CH₃), 2.74 (t, 2H, CH₃), 3.44 (s, 6H, NCH₃), 3.45 (q, 4H, NCH₃), 6.78 (dd, 1H, CH_aryl), 6.80 (s, 1H, CH_aryl), 7.37 (d, 1H, CH_aryl), 7.54 (s, 1H, CH_aryl), 8.48 (s, 1H, CH)
26o	2.95 (t, 2H, CH₂), 3.13 (t, 2H, CH₂), 3.34 (s, 3H, NCH₃), 3.39 (s, 3H, NCH₃), 3.51 (s, 3H, NCH₃), 3.55 (s, 3H, NCH₃), 7.42 (s, 1H, CH_aryl), 7.50 (dd, 1H, CH_aryl), 7.64 (s, 1H, CH_aryl), 7.65 (d, 1H, CH_aryl), 8.37 (s, 1H, CH), 8.85 (s, 1H, CH), 11.81 (s, 1H, NH)
26p	1.75 (q, 2H, CH₂), 2.69 (t, 2H, CH₂), 2.77 (t, 2H, CH₂), 3.27 (s, 3H, NCH₃), 3.37 (s, 3H, NCH₃), 3.53 (s, 3H, NCH₃), 3.60 (s, 3H, NCH₃), 7.39 (dd, 1H, CH_aryl), 7.47 (s, 1H, CH_aryl), 7.57 (s, 1H, CH_aryl), 7.65 (d, 1H, CH_aryl), 8.63 (s, 1H, CH), 8.80 (s, 1H, CH), 11.27 (s, 1H, NH)

[a]) measured in CD₃NO₂

As expected, all the benzopyrylium perchlorates **25** and **26** prepared are deeply colored compounds with intense maxima in the visible range. Whereas the 2-(aryl-alkenyl)-benzopyrylium perchlorates **25** absorb, depending upon the substitution pattern at their aryl as well as their benzopyrylium moieties, between 420 and

Tab. 9 Elemental analysis data of 2-(2-Aryl-ethenyl)-benzopyrylium-perchlorates **25**

Entry	Formula (m.w.)	C	H	N
		(found/calcd.)		
25a	$C_{19}H_{17}ClO_5$ (360.79)	62.98 / 63.25	5.87 / 4.75	
25b	$C_{21}H_{19}ClO_5$ (386.83)	64.89 / 65.20	5.27 / 4.95	
25c	$C_{24}H_{19}ClO_5$ (422.86)	67.63 / 68.17	4.77 / 4.53	
25d	$C_{24}H_{21}ClO_5$ (436.89)	68.25 / 68.73	5.13 / 4.84	
25e	$C_{24}H_{26}ClNO_5$ (443.93)	64.57 / 64.93	6.23 / 5.90	3.09 / 3.16
25f	$C_{20}H_{19}ClO_6$ (390.82)	61.21 / 61.47	5.15 / 4.90	
25g	$C_{22}H_{21}ClO_6$ (416.86)	62.97 / 63.39	5.28 / 5.08	
25h	$C_{24}H_{19}ClO_6$ (438.86)	65.53 / 65.68	4.52 / 4.36	
25i	$C_{25}H_{21}ClO_6$ (452.89)	66.12 / 66.30	5.09 / 4.87	
25j	$C_{26}H_{23}ClO_6$ (466.92)	66.76 / 66.88	5.13 / 4.97	
25k	$C_{25}H_{28}ClN_2O_5$ (473.95)	63.02 / 63.36	6.18 / 5.95	2.90 / 2.96
25l	$C_{22}H_{24}ClNO_5$ (417.89)	63.78 / 63.23	5.87 / 5.79	3.14 / 3.35
25m	$C_{21}H_{22}ClNO_5$ (403.86)	62.11 / 62.45	5.53 / 5.49	3.32 / 3.47
25n	$C_{21}H_{20}ClNO_5$ (401.85)	67.24 / 67.57	5.83 / 5.46	2.77 / 2.92
25o	$C_{22}H_{22}ClNO_5$ (415.879)	63.31 / 63.54	5.54 / 5.33	3.27 / 3.37
25p	$C_{23}H_{24}ClNO_5$ (429.90)	63.94 / 64.26	5.72 / 5.63	3.22 / 3.26
25q	$C_{25}H_{22}ClNO_5$ (451.91)	66.37 / 66.45	5.06 / 4.91	2.98 / 3.10
25r	$C_{26}H_{24}ClNO_5$ (465.93)	66.89 / 67.02	5.26 / 5.19	2.98 / 3.01
25s	$C_{27}H_{26}ClNO_5$ (479.96)	67.24 / 67.57	5.83 / 5.46	2.77 / 2.92
25t	$C_{25}H_{29}ClN2O_5$ (472.97)	63.32 / 63.49	6.03 / 6.18	5.81 / 5.92
25u	$C_{26}H_{31}ClN2O_5$ (487.00)	63.95 / 64.13	6.41 / 6.62	5.88 / 5.75
25v	$C_{27}H_{33}ClN2O_5$ (501.02)	64.28 / 64.73	6.81 / 6.64	5.45 / 5.59

Tab. 10 Elemental analysis of 2-(2-Dimethylamino-ethenyl)-substituted Benzopyrylium Perchlorates **26** and Hydrodiperchlorates $26 \cdot HClO_4$

Entry	Formula (m.w.)	C	H	N
		(found/calcd.)		
26a	$C_{15}H_{18}ClNO_5$ (327.76)	55.03 / 54.97	5.77 / 5.54	4.05 / 4.18
26b	$C_{14}H_{16}ClNO_5$ (313.74)	53.97 / 53.60	5.08 / 5.14	4.50 / 4.46
26c	$C_{15}H_{16}ClNO_5$ (325.75)	55.51 / 55.31	5.25 / 4.95	4.19 / 4.30
26d	$C_{16}H_{18}ClNO_5$ (339.78)	56.29 / 56.56	5.56 / 5.34	4.02 / 4.12
26e	$C_{17}H_{20}ClNO_5$ (353.80)	57.67 / 57.71	5.76 / 5.70	3.73 / 3.96
26f	$C_{19}H_{18}ClNO_5$ (375.81)	60.68 / 60.72	5.19 / 4.83	3.63 / 3.73
26g	$C_{20}H_{20}ClNO_5$ (389.84)	61.60 / 61.62	5.16 / 5.17	3.44 / 3.69
26h	$C_{21}H_{22}ClNO_5$ (403.86)	62.32 / 62.45	5.70 / 5.49	3.36 / 3.47
26i	$C_{16}H_{18}ClNO_6 \cdot CH_3OH$ (355.78)	52.44 / 52.65	5.82 / 5.52	3.59 / 3.61
26j	$C_{17}H_{20}ClNO_6 \cdot CH_3OH$ (369.80)	53.43 / 53.80	5.91 / 6.02	3.57 / 3.49
26k	$C_{18}H_{22}ClNO_5$ (383.83)	56.21 / 56.33	6.10 / 5.78	3.62 / 3.62
26l	$C_{19}H_{21}ClN_2O_5$ (396.87)	58.16 / 57.50	6.49 / 6.35	6.83 / 7.06
26m	$C_{20}H_{23}ClN_2O_5$ (410.90)	58.06 / 58.46	6.62 / 6.62	6.50 / 6.82
26n	$C_{21}H_{25}ClN_2O_5$ (424.92)	58.75 / 58.36	6.96 / 6.88	6.20 / 6.59
26o	$C_{18}H_{22}ClN_3O_5 \cdot CH_3OH$ (395.84)	52.93 / 53.33	6.64 / 6.12	9.72 / 9.82
26p	$C_{19}H_{24}ClN_3O_5 \cdot CH_3OH$ (409.87)	54.66 / 54.36	6.60 / 6.39	9.52 / 9.51

720 nm, the 2-dimethylamino-alkenyl-substituted benzopyrylium perchlorates **26** absorb intensively between 440 and 580 nm. In contrast to the 2-(aryl-alkenyl)-benzopyrylium perchlorates **25** which fluoresce in several cases and under specific conditions only, most of the 2-dimethylamino-alkenyl-substituted benzopyrylium perchlorates **26** fluoresce very strongly under standard conditions. Very remarkably, the fluorescence quantum yields of the 7-diethylamino- and 7-formamidino-substituted 2-dimethylamino-alkenyl-benzopyrylium perchlorates **26l–26p** are, in most cases, approximately 100%.

Experimental

Melting points were determined by means of a Boëtius heating-table microscope and are uncorrected. The IR spectra were recorded in potassium bromide pellets with a Philips FTIR spectrometer PU 9624, the visible and near infrared spectra with a Shimadzu spectrometer UV 3101, and the NMR spectra with a Varian 300 MHz spectrometer Gemini 300 or with a JEOL 200 MHz spectrometer JNM FX 200. The elemental analytical data are estimated by means of a LECO analyser CHNS 932.

2-Dialkylamino-2H-5,6-benzo[b]pyrans (14) (General Procedure):

An equimolar amount of an aliphatic or alicyclic ketone and a secondary aliphatic amine (0.2 mol), preferably pyrrolidine,

are refluxed in toluene with a Dean–Stark trap to give enamines **9**. To a refluxing solution of **9** in toluene is added a 2-hydroxy-benzaldehyde **1** (0.2 mol). After complete addition, and the separation of the appropriate amount of water (0,2 mol) the mixture is concentrated *in vacuo*, and subsequently cooled to give oily products (see Tab. 1) which are used without further purification.

2-(N-Pyrrolidino)-2,3-dimethylene-2H-naphtho[2,1-b]pyran

14g: *m.p.* 118–119 °C; yield 95% – ¹H NMR, δ-values (in toluene-d$_8$): 1.33 (m, 4H, CH$_2$), 1.48 (quintett, 2H, CH$_2$), 2.39 (t, 2H, CH$_2$), 2.57 (m, 4H, NCH$_2$), 2.90 (t, 2H, CH$_2$), 6.77 (s, 1H, CH), 7.09 (t, 1H, CH), 7.10 (d, 1H, CH), 7.24 (t, 1H, CH), 7.32 (d, 1H, CH), 7.48 (t, 1H, CH) 7.78 (d, 1H, CH); C$_{20}$H$_{21}$NO   calcd.: C 82.44   H 7.26   N 4.81   O 5.49 (291.4)   found: C 82.60   H 7.03   N 4.79   O 5.32.

2-Alkylidene-2*H*-benzo[b]pyrans (15) or their Dimers (17) (General Procedure)

Acetic anhydride (0.2 mol) is added with stirring and cooling, to a concentrated acetonitrile solution of 2-dialkylamino-2*H*-5,6-benzo[*b*]pyran **14** (0.2 mol). The reaction if left standing at room temperature before adding ethanol (50 ml), and the benzopyran products start to crystallise from the resulting mixture. They are isolated by filtration and used without further manipulations.

Benzo[*b*]pyrylium Perchlorates (16) and 2-(2-Hydroxyar-yl-ethenyl)-1-benzo[*b*] pyrylium perchlorates (23) (General Procedure)

From 2H-Benzo[b]pyrans **14** (Method A in Tab. 1):

Aqueous perchloric acid (70%, two equivalents) were added to a cooled, stirred etheral solution of a 2*H*-benzo[*b*]pyran **14**, followed by addition of acetic anhydride (two equivalents). The product which crystallised after standing in an refrigerator (see Tab. 1) is isolated by filtration and washed with ether and ethyl acetate.

From 2-Alkylidene-2H-benzo[b]pyrans **15** (Method A in Tab. 1):

A water-free solution of perchloric acid was prepared by addition of aqueous perchloric acid (70%, 0.1 mol) to acetic anhydride (50 ml) in ether at 0 °C. This solution is added to a solution of 2-alkylidene-2*H*-benzo[*b*]pyran **14** (0.1 mol) in ether (150 ml). The benzopyrylium perchlorate **16**, so formed, crystallise from the cooled reaction mixture, and can be isolated by filtration and washing with ether and ethyl acetate.

From 2-Alkylidene-2H-benzo[b]pyrans **15** (Method B in Tab. 1):

The procedure is the same as described before, however, aqueous perchloric acid (70%) is used instead of the perchloric acid in a water-free, etheral acetic acid/acetic anhydride mixture. The benzopyrylium perchlorates **16** or 2-(2-hydroxy-arylethenyl)-1-benzo[*b*]pyrylium perchlorates **23**, so formed, (see Tab. 1) crystallise from the reaction mixture upon standing. These products can be isolated by filtration and purified by recrystallisation from acetic acid or acetonitrile.

In addition to the benzo[*b*]pyrylium perchlorates **16**

analytically described in the Tab. 1, 4, and 5, the following 2-(2-hydroxyarylethenyl)-1-benzo[*b*]pyrylium perchlorates **23** have been prepared by this method:

1-(4-Diethylamino-2-hydroxybenzylidene]-7-diethylamino-cyclopenta[b]benzo[e] pyrylium perchlorate (**23a**)

m.p. 189–192 °C; yield 40%; λ_{max}/nm (log ε) (in acetic acid): 727, 4.90 – ¹H NMR, δ-values [in CD$_3$NO$_2$]: 1.20 (t, 6H, CH$_3$), 1.26 (t, 6H, CH$_3$), 3.12 (t, 4H, CH$_2$), 3.45 (q, 4H, NCH$_2$), 3,60 (q, 4H, NCH$_2$), 6.25 (s, 1H, CH), 6.40 (d, 1H, CH), 6.97 (s, 1H, CH), 7.06 (d, 1H, CH), 7.54 (d, 2H, CH), 7.84 (s, 1H, CH), 8.11 (s, 1H, CH), 12.48 (s, 1H, OH). C$_{27}$H$_{33}$ClN$_2$O$_6$ calcd.: C 62.72   H 6.43   N 5.42   Cl 6.86 (517.02)   found: C 62.21   H 6.56   N 4.93   Cl 7.16

1-(4-Diethylamino-2-hydroxybenzylidene)-8-diethylamino-cyclohexa[b]benzo[e] pyrylium perchlorate (**23b**)

m.p. 200–202 °C; yield 37%; λ_{max}/nm (log ε) (in acetic acid) 710, 4.96. – ¹H NMR, δ-values [in DMSO-D$_6$]: 1.14 (t, 6H, CH$_3$), 1.20 (t, 6H, CH$_3$), 1.83 (m, 2H, CH$_2$), 2.80 (t, 2H, CH$_2$), 2.87 (t, 2H, CH$_2$), 3.41 (q, 4H, NCH$_2$),3.62 (q, 4H, NCH$_2$), 6.24 (s, 1H, CH), 6.38 (d, 1H, CH), 6.95 (s, 1H, CH), 7.21 (d, 1H, CH), 7.49 (d, 1H, CH), 7.73 (d, 1H, CH), 8.19 (s, 1H, CH), 8.38 (s, 1H, CH), 10.44 (s, 1H, OH); C$_{28}$H$_{35}$ClN$_2$O$_6$ (531.05) found C 62.54, H 6.93, N 5.12; calcd. C 63.33, H 6.64, N 5.28.

1-(2-Hydroxy-4-methoxybenzylidene)-7-methoxy-cyclo-penta[b]benzo[e]pyrylium perchlorate (**23d**)

m.p. 193–95 °C; yield 45%; λ_{max}/nm (log ε) (in acetic acid): 585, 4.87. C$_{21}$H$_{19}$ClO$_8$ calcd.: C 57.95   H 4.37 (434.83)   found: C 57.82   H 4.77.

1-(2-Hydroxy-4-methoxybenzylidene)-8-methoxy-cyclo-hexa[b]benzo[e]pyrylium perchlorate (**23e**)

m.p. 177–180 °C; yield 20%; λ_{max}/nm (log ε) (in acetic acid): 564 , 4.85. C$_{22}$H$_{21}$ClO$_8$ calcd.: C 58.82   H 4.68 (448.85)   found: C 58.79   H 4.32.

2-(Aryl-alkenyl)-benzopyrylium Perchlorates (25) (General Procedure)

Benzopyrylium perchlorate **16** (0.01 mol), freshly prepared from their 2-alkylidene-2*H*-benzo[*b*]pyran precursors **15** by means of one of the previous methods, is added to a solution of an appropriate aromatic aldehyde (0.012 mol) in acetic anhydrid (30 ml). The resulting mixture is heated at elevated temperatures for a short time until a deeply colored solution is formed, and subsequently cooled to room temperature. The products formed (see Tab. 6) crystallise and are isolated by filtration.

2-(2-Dimethylamino-ethenyl)-substituted Benzopyrylium Perchlorates (26) (General Procedure)

Method A: POCl$_3$ (0.6 mol) is added to a cooled, stirring solution of 2-dialkylamino-2*H*-5,6-benzo[*b*]pyran **14** (0.2 mol) in DMF (0.6 mol). After stirring at room temperature the resulting mixture is poured into methanol (250 ml) containing perchloric acid (70%, 0.2 mol). The products, which crystallise

after the addition of ether, are isolated by filtration and recrystallized from acetic acid.

Method B: This method is identical to Method A, except that methanolic perchloric acid (a methanolic solution of magnesium perchlorate) is used for transforming the primary 2-(2-dimethylamino-ethenyl)-substituted benzopyrylium chlorides into the corresponding perchlorates. Moreover, aqueous ammonia is added to the resulting mixture for neutralisation of the excess of acids.

Method C: This method initially the same as Method A, and so far as 2-dialkylamino-2*H*-5,6-benzo[*b*]pyranes **14** with benzo substituted amino groups are used as educts, gives rise to benzopyrylium diperchlorates **16** · HClO$_4$. These salts are dissolved in methanol containing one equivalent of triethylamine. After heating the resulting mixture at 50 °C and cooling to room temperature the product crystallised, and was isolated by filtration. See Tab. 7 for the 2-(2-dimethylamino-ethenyl)-substituted benzopyrylium perchlorates **26** and hydrodiperchlorates **26** · HClO$_4$ prepared by means of one of the methods A – C.

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