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The synthesis of hitherto unknown *N*-(2-hydroxyphenyl) substituted 2-alkylamino-4,6-diarylbenzophenones **3** from 2,4,6-triarylpyrylium salts **1** and 3-alkyl-2-methylbenzoxazolium salts **2** in the presence of triethylamine in ethanol by a 2,5-[C₄+C₂] pyrylium ring transformation is reported. Structure elucidation is performed by an X-ray crystal structure determination of the benzophenone **3a**. Spectroscopic data of the transformation products and their mode of formation *via* anhydrobases of the salts **2** are discussed.

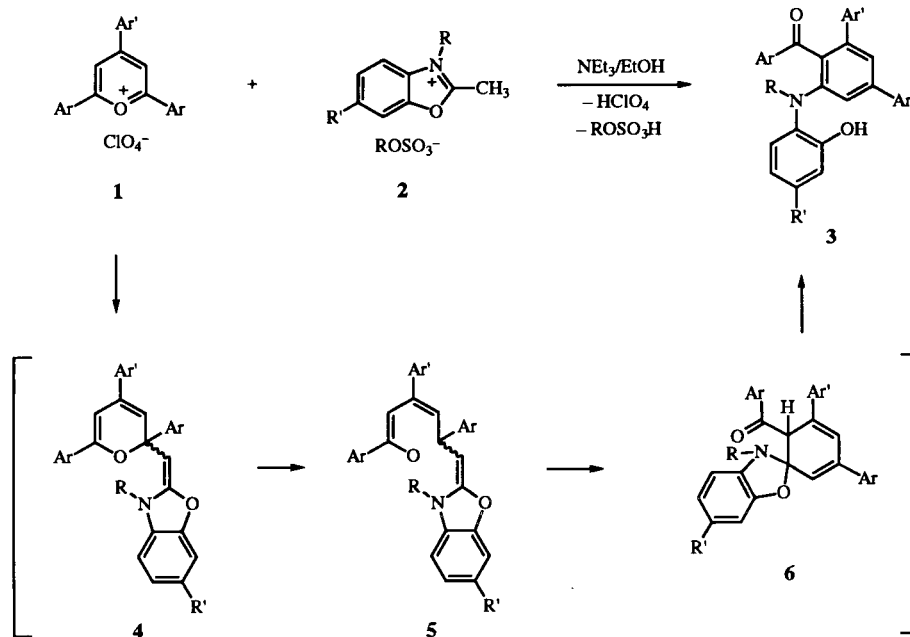
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Ring transformation reactions of 2,4,6-triarylpyrylium salts **1** [2] with heterocyclic anhydrobases of the enamine type are strongly influenced by the nature of the heterocycle used. Until now two different types of transformations have been observed. In the course of the first one a new benzene ring is built up from the five carbon atoms of the pyrylium cation and one C-atom of the anhydrobase offering a simple method for the conversion of a methyl group of a cationic nitrogen heterocycle into a 2,4,6-triarylphenyl moiety. In this way from methyl substituted pyridinium [3], bispypyridinium [4], quinolinium [5] and 1*H*-benzimidazolium [1] or benzothiazolium [1] salts the corresponding systems with a 2,4,6-triarylphenyl substituent were obtained in high yield. The second type of transformations is characterized by the formation of a cyclohexadiene ring containing only four carbon atoms of the pyrylium cation but two carbons of the anhydrobase. Thus, methyleneindolines, the anhydrobases of 3*H*-indolium salts, gave rise to spiro[cyclohexadieneindolines] which represent a novel class of photochromic substances [6,7]. Trying to extend these transformations to anhydrobases of 3-alkyl-2-methylbenzoxazolium salts [8] we surprisingly observed a different reaction pattern. In this paper we wish to report on these investigations.

When the 2,4,6-triarylpyrylium perchlorates **1** and the 3-alkyl-2-methylbenzoxazolium salts **2** were refluxed in absolute ethanol in the presence of triethylamine the *N*-(2-hydroxyphenyl) substituted 2-alkylamino-4,6-diarylbenzophenones **3** were obtained in yields up to 53%. One may assume that in the course of this transformation the

methylbenzoxazolium salts **2** are deprotonated to the corresponding anhydrobases which attack the pyrylium cation as carbon nucleophile in the preferred position 2 [2,9] to give the 2*H*-pyran derivatives **4**. Then by electrocyclic ring opening/ring closure *via* **5** the *spiro* compounds **6** are formed. In the final step an intramolecular amine elimination takes place giving rise to the benzophenones **3**. Since the benzene ring formed contains four carbon atoms of the pyrylium cation and two carbons of the nucleophile which connect the former positions 2 and 5 of the pyrylium ring it can be classified as a 2,5-[C₄+C₂] transformation [10]. Unlike the above discussed transformations of the salts **1** with methyleneindolines where spiro[cyclohexadieneindolines] are the stable end products under comparable reaction conditions [6] the related *spiro* compounds **6** are only unstable intermediates and hence instead of these cyclohexadiene derivatives the benzophenones **3** are isolated. In case of the spiro[cyclohexadieneindolines] an intramolecular amine elimination to 2-[1-methyl-1-(2-phenylamino-phenyl)ethyl] substituted benzophenones, comparable to the elimination **6**→**3**, can only be achieved by treatment with strong acids in a separate reaction step [6].

For an unequivocal structure elucidation of the benzophenones **3** an X-ray crystal structure determination of the compound **3a** was performed. Figure 1 shows the ellipsoid drawing of the molecular structure of **3a** and the atomic numbering scheme; the crystal data collection parameters and structure refinement parameters, fractional position parameters and equivalent thermal parameters as well as selected bond lengths and angles are summarized



1	2	Ar	Ar'	R	R'	3
a	a	Ph	Ph	Me	H	a
b	a	Ph	4-Me-C ₆ H ₄	Me	H	b
c	a	Ph	4-Cl-C ₆ H ₄	Me	H	c
d	a	Ph	4-Br-C ₆ H ₄	Me	H	d
e	a	4-Me-C ₆ H ₄	Ph	Me	H	e
f	a	4-Cl-C ₆ H ₄	Ph	Me	H	f
g	a	4-Br-C ₆ H ₄	Ph	Me	H	g
a	b	Ph	Ph	Et	H	h
a	c	Ph	Ph	Me	Me	i
a	d	Ph	Ph	Me	Ph	j

Table 1

Physical and Analytical Data for the 2-[N-Alkyl-N-(2-hydroxyphenyl)amino]-4,6-diarylbenzophenones 3

No.	-benzophenone	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	C	Analysis (%)		
						Calcd.	Found	N
3a	2-[N-(2-Hydroxyphenyl)-N-methylamino]-4,6-diphenyl-	44	189-190	C ₃₂ H ₂₅ NO ₂ (455.6)	84.37	5.53	3.07	
					84.30	5.55	3.11	
3b	2-[N-(2-Hydroxyphenyl)-N-methylamino]-6-(4-methylphenyl)-4-phenyl-	37	221-222	C ₃₃ H ₂₇ NO ₂ (469.6)	84.41	5.80	2.98	
					84.38	5.74	3.02	
3c	2-(4-Chlorophenyl)-6-[N-(2-hydroxyphenyl)-N-methylamino]-4-phenyl-	42	235-236	C ₃₂ H ₂₄ ClNO ₂ (490.0)	78.44	4.94	2.86	
					78.35	4.95	2.88	
3d	2-(4-Bromophenyl)-6-[N-(2-hydroxyphenyl)-N-methylamino]-4-phenyl-	42	233-234	C ₃₂ H ₂₄ BrNO ₂ (534.5)	71.92	4.53	2.62	
					72.00	4.53	2.65	
3e	2-[N-(2-Hydroxyphenyl)-N-methylamino]-4'-methyl-4-(4-methylphenyl)-6-phenyl-	26	146-148	C ₃₄ H ₂₉ NO ₂ (483.6)	84.44	6.04	2.90	
					84.53	6.05	2.85	
3f	4'-Chloro-4-(4-chlorophenyl)-2-[N-(2-hydroxyphenyl)-N-methylamino]-6-phenyl-	14	177-179	C ₃₂ H ₂₃ Cl ₂ NO ₂ (524.5)	73.29	4.42	2.67	
					73.35	4.42	2.70	
3g	4'-Bromo-4-(4-bromophenyl)-2-[N-(2-hydroxyphenyl)-N-methylamino]-6-phenyl-	37	195-197	C ₃₂ H ₂₃ Br ₂ NO ₂ (613.4)	62.66	3.78	2.28	
					62.73	3.75	2.25	
3h	2-[N-Ethyl-N-(2-hydroxyphenyl)amino]-4,6-diphenyl-	35	152-153	C ₃₃ H ₂₇ NO ₂ (469.6)	84.41	5.80	2.98	
					84.49	5.75	3.05	
3i	2-[N-(2-Hydroxy-4-methylphenyl)-N-methylamino]-4,6-diphenyl-	34	156-158	C ₃₃ H ₂₇ NO ₂ (469.6)	84.41	5.80	2.98	
					84.45	5.75	2.98	
3j	2-[N-(2-Hydroxy-4-phenylphenyl)-N-methylamino]-4,6-diphenyl-	53	228-229	C ₃₈ H ₂₉ NO ₂ (531.7)	85.85	5.50	2.63	
					85.84	5.45	2.63	

Table 2
Spectral Data for the 2-[*N*-Alkyl-*N*-(2-hydroxyphenyl)amino]4,6-diarylbenzophenones 3

Compound	IR (KBr) (cm ⁻¹) CO, OH	UV (CH ₃ CN) λ _{max} (nm) (log ε)	¹ H-NMR (DMSO-d ₆) [a] δ (ppm)
3a [b][c]	1653, 3443	250 (4.64)	3.06 (s, 3H, NCH ₃), 6.40-7.69 (m, 21H, arom-H), 8.89 (s, 1H, OH)
3b	1655, 3452	252 (4.68)	2.09 (s, 3H, CH ₃), 3.05 (s, 3H, NCH ₃), 6.41-7.66 (m, 20H, arom-H), 8.88 (s, 1H, OH)
3c	1652, 3458	252 (4.67)	3.07 (s, 3H, NCH ₃), 6.39-7.69 (m, 20H, arom-H), 8.93 (s, 1H, OH)
3d	1652, 3460	253 (4.70)	3.07 (s, 3H, NCH ₃), 6.39-7.77 (m, 20H, arom-H), 8.91 (s, 1H, OH)
3e [c]	1651, 3449	256 (4.66)	2.18 (s, 3H, CH ₃), 2.27 (s, 3H, CH ₃), 3.03 (s, 3H, NCH ₃), 6.45-7.77 (m, 19H, arom-H), 8.87 (s, 1H, OH)
3f	1652, 3449	256 (4.65)	3.09 (s, 3H, NCH ₃), 6.36-7.76 (m, 19H, arom-H), 8.92 (s, 1H, OH)
3g	1648, 3438	259 (4.66)	3.08 (s, 3H, NCH ₃), 6.36-7.70 (m, 19H, arom-H), 8.92 (s, 1H, OH)
3h	1653, 3310	250 (4.65), 287 sh (4.26)	0.87 (t, 3H, CH ₃), 3.53 (q, 2H, NCH ₂), 6.43-7.67 (m, 21H, arom-H), 8.82 (s, 1H, OH)
3i	1662, 3438	249 (4.67), 287 sh (4.28)	1.84 (s, 3H, CH ₃), 3.05 (s, 3H, NCH ₃), 6.36-7.71 (m, 20H, arom-H), 8.73 (s, 1H, OH)
3j [c]	1658, 3438	253 (4.79)	3.16 (s, 3H, NCH ₃), 6.51-7.72 (m, 25H, arom-H), 9.14 (s, 1H, OH)

[a] Arom-H denotes the protons bonded to the benzene rings. [b] ¹³C nmr: 40.0 (NCH₃), 113.8, 116.5, 117.0, 119.8, 122.7, 123.2, 124.9, 125.1, 125.7, 125.8, 125.9, 126.9, 127.0, 128.7, 130.6, 134.4, 134.9, 137.6, 138.2, 139.4, 147.9, 149.5 (carbons of the benzene rings), 194.7 (CO). [c] Mass spectra: (70 eV), m/z (%) 3a 455 (39) [M⁺], 437 (100) [M⁺ - H₂O], 105 (12) [PhCO⁺], 77 (11) [Ph⁺], 3e 470 (30) [M⁺], 451 (100) [M⁺ - H₂O], 105 (18) [PhCO⁺], 77 (16) [Ph⁺], 3j 531 (41) [M⁺], 513 (100) [M⁺ - H₂O], 105 (36) [PhCO⁺], 77 (38) [Ph⁺].

in the Tables 3-5. As expected the benzene rings of 3a are not arranged in one plane. Since sterical overcrowding in the positions 1, 2 and 6 is higher than in position 4, the phenyl substituents bonded to the nitrogen, the carbonyl group and at C-6 are more twisted relative to the plane of

the central benzene unit (twisting angles: 78.99°, 71.12°, 50.12°) than the one at C-4 (twisting angle: 30.56°).

The results of the elemental analyses and the spectroscopic data (*cf.* Tables 1 and 2) are in agreement with the structure of the *N*-(2-hydroxyphenyl) substituted 2-alkyl-amino-4,6-diarylbenzophenones 3. In the ¹H nmr spectra the *N*-bonded methyl group of 3a-g/3i,j and the OH-protons cause singulets at 3.03-3.16 ppm and 8.73-9.14 ppm, respectively; the aromatic protons resonate at 6.36-7.77 ppm with the expected pattern. The ¹³C nmr spectrum,

Table 3
Crystal Data Collection and Structure Refinements Parameters

Crystal dimensions (mm ³)	0.50 x 0.05 x 0.05
Formula	C ₃₂ H ₂₅ NO ₂
M	455.53
Crystal system/Space group	Monoclinic/P2 ₁ /n
Unit cell dimensions	a = 6.197(1) Å b = 26.075(2) Å c = 14.524(2) Å β = 93.37(1)°
V (Å ³)	2342.8(5)
Z	4
D _c (g cm ⁻³)	1.291
Radiation (λ)	CuKα (1.54184 Å)
F(000)	960
Data collection method	ω - scans
Linear absorption coefficient (mm ⁻¹)	0.627
Weighting scheme	1/(σ ² (F _o) ² +0.0607P ² +0.0283P) with P = (F _o ² +2F _c ²)/3
Reflections measured	5023
θ range (°)	5.94-64.99
Range of h, k and l	h: -1→6, k: 0→30, l: -17→17
Independent reflections/R _{int}	3827/0.0305
Independent reflections (I>2σ(I))	2657
Parameter refined	416
R ₁ (obs)/R ₁ (all refl.)	0.045/0.083
wR2(obs)/wR2(all refl.)	0.102/0.119
Goof (F ²)	1.052
Programs used	SHELXS-86 [12], SHELXL-93 [13], PLATON [14], HELENA [14]

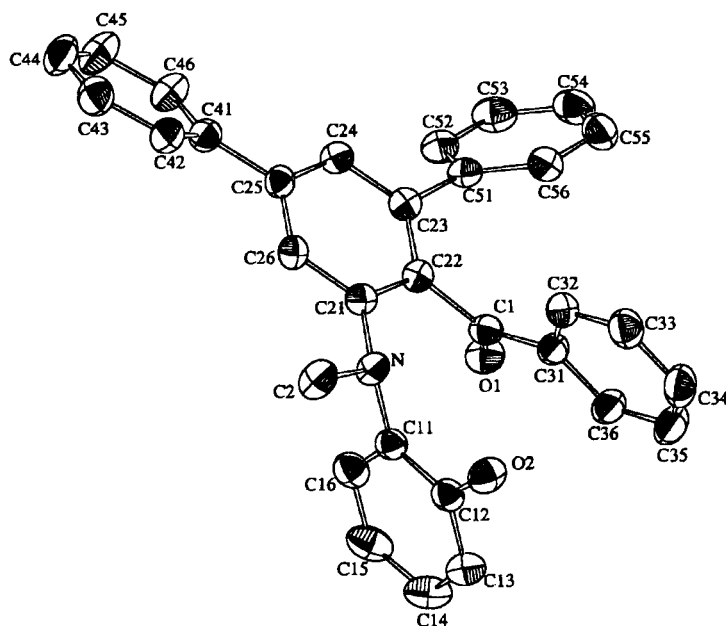


Figure 1. Ellipsoid drawing [11] of the molecular structure of the benzophenone 3a together with the atomic numbering scheme.

Table 4

Fractional Positional Parameters ($\cdot 10^4$) and Equivalent Thermal Parameter ($\text{\AA}^3 \cdot 10^3$) for the Benzophenone **3a**

	x	y	z	U(eq)
O(1)	603(3)	1233(1)	1906(1)	38(1)
O(2)	7830(3)	753(1)	3115(1)	38(1)
N	6164(3)	1747(1)	2786(1)	30(1)
C(1)	2446(4)	1301(1)	1673(1)	30(1)
C(2)	8066(4)	1990(1)	3250(2)	40(1)
C(11)	5136(3)	1398(1)	3385(1)	28(1)
C(12)	6031(4)	912(1)	3526(1)	31(1)
C(13)	3247(4)	707(1)	4544(2)	47(1)
C(14)	5076(4)	569(1)	4108(2)	40(1)
C(15)	2393(4)	1195(1)	4429(2)	45(1)
C(16)	3344(4)	1536(1)	3858(2)	36(1)
C(21)	4864(3)	2060(1)	2180(1)	27(1)
C(22)	3207(3)	1849(1)	1590(1)	28(1)
C(23)	2044(4)	2174(1)	962(1)	30(1)
C(24)	2499(4)	2695(1)	944(2)	32(1)
C(25)	4076(4)	2909(1)	1548(1)	29(1)
C(26)	5235(4)	2587(1)	2156(2)	31(1)
C(31)	3847(4)	862(1)	1454(1)	30(1)
C(32)	5804(4)	931(1)	1043(2)	35(1)
C(33)	7047(5)	511(1)	834(2)	42(1)
C(34)	6361(5)	23(1)	1036(2)	48(1)
C(35)	4406(5)	-48(1)	1444(2)	49(1)
C(36)	3150(4)	367(1)	1650(2)	39(1)
C(41)	4503(4)	3468(1)	1574(2)	32(1)
C(42)	6561(4)	3659(1)	1837(2)	38(1)
C(43)	6924(5)	4181(1)	1905(2)	45(1)
C(44)	5281(5)	4527(1)	1706(2)	51(1)
C(45)	3256(5)	4342(1)	1429(2)	51(1)
C(46)	2868(4)	3823(1)	1361(2)	42(1)
C(51)	378(4)	171(1)	270(1)	30(1)
C(52)	-1633(4)	211(1)	157(2)	36(1)
C(53)	-3165(4)	2038(1)	-511(2)	44(1)
C(54)	-2709(5)	1632(1)	-1074(2)	46(1)
C(55)	-715(4)	1392(1)	-977(2)	43(1)
C(56)	811(4)	1561(1)	-307(2)	35(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

recorded for the benzophenone **3a**, shows the singulett of the carbonyl carbon at 194.7 ppm. A characteristic feature of the ir spectra are the absorptions at 1648-1662 cm^{-1} (CO-vibration) and at 3310-3460 cm^{-1} (OH-vibration). Finally, in the uv spectra a strong absorption band caused by the aromatic π -system at 249-259 nm can be observed.

Table 5

Selected Bond Lengths and Angles in the Benzophenone **3a**

Bond Lengths [\AA]

O1 - C1	1.223(3)	O2 - C12	1.360(3)
C1 - C31	1.483(3)	C1 - C22	1.511(3)
N - C2	1.467(3)	N - C11	1.434(3)
N - C21	1.416(3)	C23 - C51	1.495(3)
C25-C41	1.481(3)		

Bond Angles [$^\circ$]

O1 - C1 - C22	117.5(2)	O1 - C1 - C31	121.0(2)
C22-C1-C31	108.9(2)	C2-N-C21	116.7(2)
C2-N-C11	111.7(2)	C11-N-C21	119.1(2)

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 (199.975 MHz for protons, 50.289 MHz for ^{13}C nuclei, DMSO- d_6 , 25 $^\circ$, HMDSO as the 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 $^\circ$). Mass spectra were determined on a Finnigan MAT 111 A spectrometer (70 eV, electron impact). The pyrylium perchlorates **1a** [15], **1b** [16], **1c** [17], **1d** [18] and **1e-g** [19] were prepared according to literature procedures; the benzoxazolium salts **3** were synthesized by alkylation of 2-methylbenzoxazoles, purchased from Aldrich, with dialkyl sulfates as described in ref [20].

Preparation of *N*-(2-Hydroxyphenyl) Substituted 2-Alkylamino-4,6-diaryl-benzophenones **3** from 2,4,6-Triarylpyrylium Perchlorates **1** and 3-Alkyl-2-methylbenzoxazolium Salts **2**. General Procedure (cf. Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate **1**, 5 mmoles benzoxazolium salt **2** and triethylamine (1.51 g, 15 mmoles) were added. The reaction mixture was then refluxed for 2 hours. The benzophenones **3** formed crystallized in some cases from the hot reaction mixture; otherwise their crystallization was initiated by cooling. They were filtered off by suction, washed with ethanol and recrystallized from ethanol/xylene.

X-Ray Structure Determination.

Appropriate crystals of the benzophenone **3a** were obtained by slow cooling of an ethanol/xylene solution. X-ray data were collected on an Enraf-Nonius CAD 4 diffractometer at -70 $^\circ$. The unit cell dimensions were determined from the angular setting of 25 high angle reflections. No absorption correction was applied. The structure was solved by direct methods [12]. Refinement was performed with SHELXL-93 [13]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen positions could be located from successive Fourier maps and were included in the structure refinement. The final difference Fourier map showed maximum electron density peaks and holes of 0.151 $\text{e} \cdot \text{\AA}^{-3}$ and -0.239 $\text{e} \cdot \text{\AA}^{-3}$, respectively. Further details of the X-ray data collection and structure calculation can be derived from Table 3. Table 4 contains the atomic positions and Table 5 selected bond lengths and angles.

The results of the crystal structure determination (full list of bond lengths and angles, anisotropic thermal parameters and hydrogen atom positions) have been deposited with the Fachinformationszentrum, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, as Supplementary Publication No CSD 405199.

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