# Ring Transformations of Heterocyclic Compounds. **XXV** [1].
Phenanthrene Aldehyde Imines Via Ring Transformation of Pyrylium Salts with Methylenedihydroisoquinolines – A Novel Access to the Phenanthrene Skeleton

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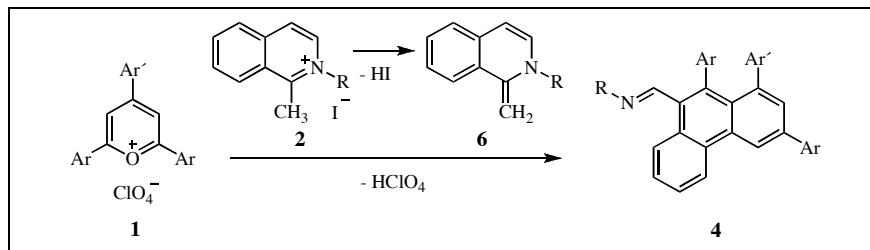
The ring transformation of 2,4,6-triarylpyrylium salts **1** with 2-methylenedihydroisoquinolines **6**, generated *in situ* from the related 2-methylisoquinolinium salts **2**, in the presence of bases is reported. Whereas the transformation of **1** with **2(6)** and sodium methoxide in methanol leads to 2-(2,4,6-triarylphenyl)isoquinolinium salts, with sodium ethoxide in ethanol the aryl substituted phenanthrene-9-carbaldehyde imines **4** are obtained, the structure of which was confirmed by an X-ray structure determination of the 1-(4-methylphenyl) substituted derivative. Acid catalyzed hydrolysis of the imines **4** gives rise to the parent phenanthrene aldehydes. The transformation **1** + **2(6)** → **4** represents a novel access to the phenanthrene skeleton.

Since the discovery of ring transformations of pyrylium salts with carbon nucleophiles [2] these reactions have been established as a valuable tool in organic chemistry for the synthesis of a wide range of carbocyclic as well as heterocyclic compounds otherwise often difficult or not available [3].

In recent years we have systematically studied transformations of 2,4,6-triarylpyrylium salts **1** with five- and six-membered exomethylene azaheterocycles, the deprotonation products of the related methyl substituted cationic N-heterocycles (in the older literature called "anhydrobases"). Depending on the structure of the products obtained, the transformations can be classified into three types. The first type is characterized by the formation of a cyclohexadiene ring from four of the five carbon atoms of the pyrylium moiety and two C-atoms of the nucleophile. It has been observed in the reaction of the salts **1** with methyleneindolines [1,4], their spiro-connected [5] and benzo-fused [6] derivatives and with methylenedihydroacridines [7] giving rise to spiro-[cyclohexadiene-indolines] and spiro[cyclohexadiene-dihydroacridines], respectively, which represent first examples of a novel class of photochromic compounds, the spiro[cyclohexadiene-azaheterocycles] [8,9]. The transformation of the salts **1** with methylenedihydro-benzoxazoles to aryl substituted aminobenzophenones is the only known example for the second type, in which instead of a cyclohexadiene a benzene ring is built up

[10]. A characteristic feature of the third type is a new formed benzene ring containing not only four but all the five C-atoms of the pyrylium system and one C from the carbon nucleophile. Such transformation has been observed when the salts **1** were treated with *in situ* generated methylenedihydropyridines [11], -quinolines [12], -benzimidazolines [13], -benzothiazolines [13], -imidazolidines [14] and -thiazolidines [14] to give 2,4,6-triarylphenylpyridinium, -quinolinium, -benzimidazolium, -benzothiazolium, -imidazolium and -thiazolium salts. In continuation of these investigations we now have become interested in reactions of the 2,4,6-triarylpyrylium salts **1** with methyl substituted isoquinolinium salts [15] in the presence of base. In this paper we wish to report on the results of these investigations.

When the 2,4,6-triarylpyrylium perchlorates **1a,b** were treated with the 2-methylisoquinolinium iodides **2a,b** in boiling methanol in the presence of sodium methoxide the 2-(2,4,6-triarylphenyl)isoquinolinium perchlorates **3a-c** were obtained in 56-64% yield. As in the case of the
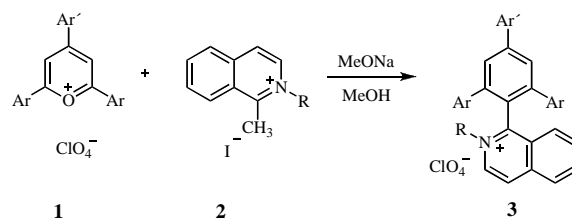
related quinolinium isomers already observed [12], this transformation offers a simple possibility for the conversion of a methyl group in 2-postion of **2** into the bulky 2,4,6-triarylphenyl substituent.

The change of the base and the solvent from sodium methoxide/methanol to sodium ethoxide/ethanol had a drastic influence on the course of the transformation and hence on the structure of the products formed. Surprisingly, when the 2,4,6-pyrylium perchlorates **1a**-**g** were treated under these conditions with the 2-methylisoquinolinium iodides **2a**-**b** instead of 2-(2,4,6-triarylphenyl)isoquinolinium derivatives of the type **3** the aryl substituted phenanthrene-9-carbaldehydes imines **4a**-**h** were isolated in 51-65% yield which can easily be

hydrolyzed with hydrochloric acid in ethanol/water to the parent aldehydes **5a**-**g**. This former unknown type of pyrylium ring transformation offers a novel access to the phenanthrene skeleton [16].

On reacting the salts **1** with the isomeric 3-methyl- or 4-methylisoquinolinium iodides in the presence of sodium methoxide in methanol or sodium ethoxide in ethanol, respectively, no transformation products could be obtained.

The structure of the phenanthrene aldehyde imines **4** was confirmed by an X-ray structure determination of the *N*-Methyl-1-[1-(4-methylphenyl)-3,10-diphenylphenanthren-9-ylmethylene]amine (**4b**). Figure 1 shows the molecular structure and Figure 2 the arrangement of two molecules in the unit cell. Besides an unequivocal proof
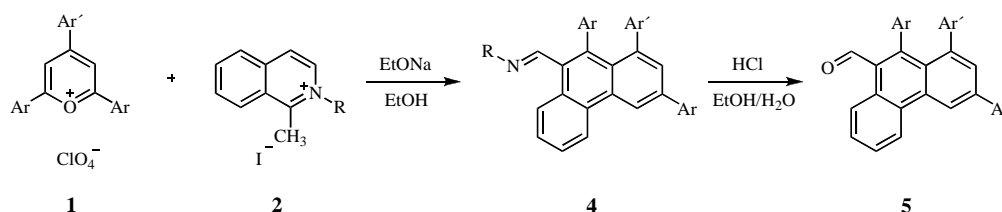
Table 1

Physical and Analytical Data for the Phenanthrene-9-carbaldehyde Imines **4** and the Phenanthrene-9-carbaldehydes **5**

No.	Compound	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found		
					C	H	N
4a	*N*-Methyl-(1,3,10-triphenylphenanthren-9-yl-methylene)amine	56	208-209	$C_{34}H_{25}N$ (447.6)	91.24 91.20	5.63 5.70	3.13 3.16
4b	*N*-Methyl-[1-(4-methylphenyl)-3,10-diphenyl-phenanthren-9-ylmethylene]amine	59	208-209	$C_{35}H_{27}N$ (461.6)	91.07 91.18	5.90 5.91	3.03 2.99
4c	[1-(4-Methoxyphenyl)-3,10-diphenyl-phenanthren-9-ylmethylene]-*N*-methylamine	57	206-207	$C_{35}H_{27}NO$ (477.6)	88.02 88.05	5.70 5.65	2.93 2.91
4d	[1-(4-Chlorophenyl)-3,10-diphenylphenanthren-9-ylmethylene]-*N*-methylamine	64	173-174	$C_{34}H_{24}ClN$ (482.0)	84.72 84.80	5.02 5.03	2.91 2.95
4e	[1-(4-Bromophenyl)-3,10-diphenylphenanthren-9-ylmethylene]-*N*-methylamine	65	213-214	$C_{34}H_{24}BrN$ (526.5)	77.57 77.50	4.59 4.62	2.66 2.72
4f	*N*-Methyl-[3,10-bis(4-methylphenyl)-1-phenyl-phenanthren-9-ylmethylene]amine	51	171-172	$C_{36}H_{29}N$ (475.6)	90.91 90.80	6.15 6.18	2.94 2.91
4g	[3,10-Bis(4-chlorophenyl)-1-phenylphenanthren-9-ylmethylene]-*N*-methylamine	65	189-190	$C_{34}H_{23}Cl_2N$ (516.5)	79.07 79.10	4.49 4.50	2.71 2.75
4h	*N*-Ethyl-(1,3,10-triphenylphenanthren-9-ylmethylene)amine	51	183-184	$C_{35}H_{27}N$ (461.6)	91.07 91.06	5.90 5.85	3.03 3.10
5a	1,3,10-Triphenylphenanthrene-9-carbaldehyde	89 [a] 65 [b]	183-184	$C_{33}H_{22}O$ (434.5)	91.21 91.30	5.10 5.11	
5b	1-(4-Methylphenyl)-3,10-diphenylphenanthrene-9-carbaldehyde	84	177-178	$C_{34}H_{24}O$ (448.6)	91.04 90.99	5.39 5.28	
5c	1-(4-Methoxyphenyl)-3,10-diphenyl-phenanthrene-9-carbaldehyde	83	209-210	$C_{34}H_{24}O_2$ (464.6)	87.90 87.80	5.21 5.23	
5d	1-(4-Chlorophenyl)-3,10-diphenyl-phenanthrene-9-carbaldehyde	86	208-209	$C_{33}H_{21}ClO$ (469.0)	84.52 84.51	4.51 4.48	
5e	1-(4-Bromophenyl)-3,10-diphenyl-phenanthrene-9-carbaldehyde	85	214-215	$C_{33}H_{21}BrO$ (513.4)	77.20 77.30	4.12 4.20	
5f	3,10-Bis(4-methylphenyl)-1-phenylphenanthrene-9-carbaldehyde	88	215-216	$C_{35}H_{26}O$ (462.6)	90.88 90.92	5.67 5.65	
5g	3,10-Bis(4-chlorophenyl)-1-phenylphenanthrene-9-carbaldehyde	65	194-195	$C_{33}H_{20}Cl_2O$ (503.4)	78.73 78.65	4.00 4.08	
5h	3,10-Bis(4-bromophenyl)-1-phenylphenanthrene-9-carbaldehyde	68	201-202	$C_{33}H_{20}Br_2O$ (592.3)	66.91 66.95	3.40 3.42	

[a] From **4a**. [b] From **4h**.

Table 2

Spectroscopic Data for the Phenanthrene-9-carbaldehyde Imines **4** and the Phenanthrene-9-carbaldehydes **5**

Comp.	UV (CH$_3$CN) λ_{max} (nm) (log ε)	IR (KBr) (cm^{-1}) C=N [b]/C=O [c]	^{13}C-NMR (CDCl$_3$) δ (ppm) C=N [b]/C=O [c]	^{1}H-NMR (DMSO-d$_6$) [a] δ (ppm)
4a [d]	271 (4.76), 329 (4.35)	1644	163.9	3.41 (d, 3H, NCH$_3$), 6.90-7.85 (m, 18H, arom-H), 7.97 (q, J = 1.6 Hz, 1H, CH=N), 8.81 (d, 1H, 8-H), 8.90 (d, 1H, 5-H), 9.02 (d, 1H, 4-H)
4b	255 sh (4.67), 271 (4.74), 329 (4.34)	1641	163.9	2.26 (s, 3H, C$_6$H$_4$CH$_3$), 3.43 (d, J = 1.8 Hz, 3H, NCH$_3$), 6.77-7.88 (m, 17H, arom-H), 7.99 (q, J = 1.8 Hz, 1H, CH=N), 8.83 (d, 1H, 8-H), 8.92 (d, 1H, 5-H), 9.04 (d, 1H, 4-H)
4c	260 sh (4.72), 270 (4.72), 328 (4.34)	1643	163.9	3.41 (d, J = 1.2 Hz, 3H, NCH$_3$), 3.75 (s, 3H, C$_6$H$_4$OCH$_3$), 6.51-7.85 (m, 17H, arom-H), 7.96 (q, J = 1.2 Hz, 1H, CH=N), 8.78 (d, 1H, 8-H), 8.90 (d, 1H, 5-H), 9.00 (d, 1H, 4-H)
4d	270 (3.73), 329 (4.33)	1643	163.8	3.41 (d, J = 1.5 Hz, 3H, NCH$_3$), 6.82-7.84 (m, 17H, arom-H), 7.98 (q, J = 1.5 Hz, 1H, CH=N), 8.80 (d, 1H, 8-H), 8.89 (d, 1H, 5-H), 9.03 (d, 1H, 4-H)
4e	271 (4.78), 331 (4.36)	1645	163.9	3.41 (d, J = 1.8 Hz, 3H, NCH$_3$), 6.76-7.83 (m, 17H, arom-H), 7.99 (q, J = 1.8 Hz, 1H, CH=N), 8.80 (d, 1H, 8-H), 8.91 (d, 1H, 5-H), 9.03 (d, 1H, 4-H)
4f	272 (4.77), 331 (4.37)	1640	164.0	2.21 (s, 3H, C$_6$H$_4$CH$_3$), 2.44 (s, 3H, C$_6$H$_4$CH$_3$), 3.42 (d, J = 1.5 Hz, 3H, NCH$_3$), 6.71-7.74 (m, 16H, arom-H), 8.02 (q, J = 1.6 Hz, 1H, CH=N), 8.84 (d, 1H, 8-H), 8.89 (d, 1H, 5-H), 9.00 (d, 1H, 4-H)
4g	273 (4.82), 330 (4.40)	1643	163.4	3.41 (d, J = 1.8 Hz, 1H, NCH$_3$), 6.75-7.76 (m, 16H, arom-H), 7.99 (q, J = 1.8 Hz, 1H, CH=N), 8.72 (d, 1H, 8-H), 8.84 (d, 1H, 5-H), 8.93 (d, 1H, 4-H)
4h	271 (4.75), 329 (4.34)	1641	161.8	1.27 (t, 3H, NCH$_2$CH$_3$), 3.54 (q, 2H, NCH$_2$CH$_3$), 6.92-7.88 (m, 18H, arom-H), 7.98 (t, 1H, NCH$_2$), 8.76 (d, 1H, 8-H), 8.93 (d, 1H, 5-H), 9.05 (d, 1H, 4-H)
5a	256 sh (4.62), 271 (4.66), 343 (4.31)	1671	196.4	6.95-7.88 (m, 18H, arom-H), 8.89 (d, 1H, 5-H), 9.03 (d, 1H, 4-H), 9.21 (d, 1H, 8-H), 9.83 (s, 1H, CHO)
5b	255 sh (4.65), 270 (4.68), 343 (4.33)	1672	196.3	2.26 (s, 3H, C$_6$H$_4$CH$_3$), 6.79-7.84 (m, 17H, arom-H), 8.85 (d, 1H, 5-H), 8.97 (d, 1H, 4-H), 9.13 (d, 1H, 8-H), 9.77 (s, 1H, CHO)
5c	254 (4.68), 270 sh (4.66), 342 (4.31)	1673	196.4	3.48 (s, 3H, C$_6$H$_4$OCH$_3$), 6.50-7.83 (m, 17H, arom-H), 8.85 (d, 1H, 5-H), 8.95 (d, 1H, 4-H), 9.09 (d, 1H, 8-H), 9.75 (s, 1H, CHO)
5d	256 sh (4.63), 270 (4.66), 343 (4.31)	1670	196.1	6.79-7.82 (m, 17H, arom-H), 8.85 (d, 1H, 5-H), 8.99 (d, 1H, 4-H), 9.11 (d, 1H, 8-H), 9.78 (s, 1H, CHO)
5e	255 sh (4.64), 270 (4.66), 343 (4.31)	1670	196.0	6.73-7.82 (m, 17H, arom-H), 8.86 (d, 1H, 5-H), 9.00 (d, 1H, 4-H), 9.08 (d, 1H, 8-H), 9.77 (s, 1H, CHO)
5f	255 sh (4.63), 273 (4.69), 346 (4.38)	1670	196.2	2.22 (s, 3H, C$_6$H$_4$CH$_3$), 2.44 (s, 3H, C$_6$H$_4$CH$_3$), 6.79-7.78 (m, 16H, arom-H), 8.84 (d, 1H, 5-H), 8.96 (d, 1H, 4-H), 9.14 (d, 1H, 8-H), 9.81 (s, 1H, CHO)
5g	256 sh (4.63), 274 (4.71), 344 (4.36)	1671	195.5	6.86-7.80 (m, 16H, arom-H), 8.85 (d, 1H, 5-H), 8.95 (d, 1H, 4-H), 9.10 (d, 1H, 8-H), 9.82 (s, 1H, CHO)

[a] 4-H, 5-H and 8-H denote the protons in 4-, 5- and 8-position of the phenanthrene moiety and arom-H the other protons of the phenanthrene moiety as well as the protons bonded to the aryl substituents. [b] For **4a-h**. [c] For **5a-g**. [d] Mass spectrum (70 eV): m/z (%) 446 (100) [M$^+$-H], 447 (48) [M$^+$].
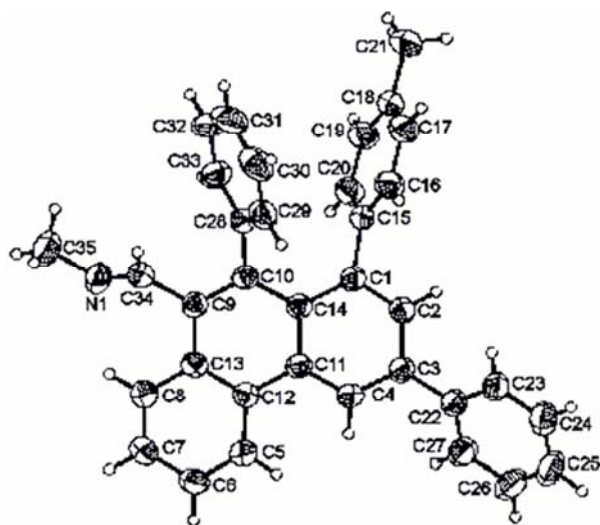

Figure 1. Ellipsoid drawing (50% probability ellipsoids) of the molecular structure of *N*-methyl-[1-(4-methylphenyl)-3,10-diphenylphenanthren-9-ylmethylene]amine (**4b**) together with the atomic numbering scheme.

of the constitution of the ring transformation products **4** the structure determination also indicated that the imino double bond has the expected *E*-configuration. Another interesting feature is the nonplanarity of the phenanthrene skeleton caused by steric interaction of the substituents 10-Ar, Ar´ and C=NR (*cf.* Figure 3). The angle between the plane of the benzene ring A (carbon atoms 1-4, 11 and 14) and ring B (carbon atoms 9-14) was measured to be 7.35(8)° and that one between B and C (carbon atoms 5, 8, 12 and 13) to be 3.85(9)°.

The results of the elemental analyses and the spectroscopic data are in agreement with the structure of the isoquinolinium salts **3**, the phenanthrene-9-carbalde-hyde imines **4** and the phenanthrene-9-carbaldehydes **5** (*cf.* Tables 1 and 2).

The nmr spectra of the salts **3a-c** show the expected pattern and the FAB mass spectra the peak of the isoquinolinium cation.

In the ^{1}H nmr spectra of the imines **4** the N-bonded methyl group of **4a-g** is responsible for the signal at 3.41-
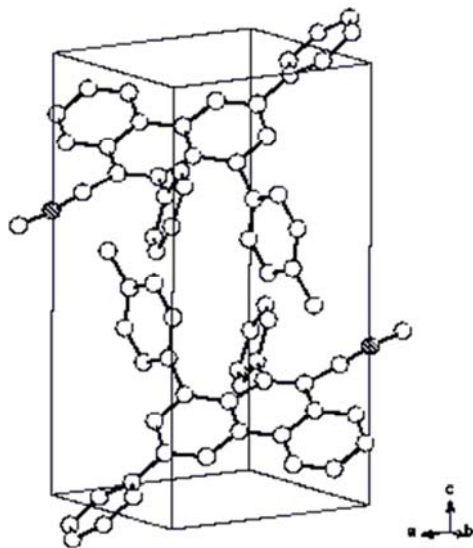
Figure 2. Unit cell of *N*-methyl-[1-(4-methylphenyl)-3,10-diphenyl-phenanthren-9-ylmethylene]amine (**4b**).
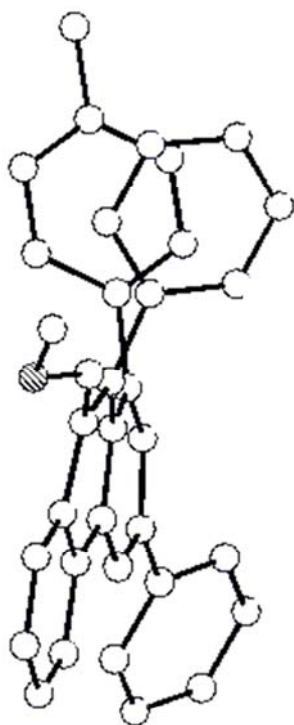

Figure 3. View on the *N*-methyl-[1-(4-methylphenyl)-3,10-diphenylphenanthren-9-ylmethylene]amine molecule (**4b**) along the phenanthrene skeleton.

3.47 ppm splitted to a doublet by coupling with the imino hydrogen (J = 1.2-1.8 Hz) which resonates at 7.96-8.02 ppm as a quartet. The presence of the imino group in **4a**-**h** is further confirmed by a strong ir absorption at 1640-1645 cm^{-1} and a ^{13}C signal at 161.8-164.0 ppm. An ir absorption band of high intensity at 1670-1673 cm^{-1}, the

formyl hydrogen ^{1}H nmr resonance at 9.75-9.83 ppm and the ^{13}C nmr signal at 195.5-196.4 ppm show that **5a**-**g** are aromatic aldehydes. The protons of the phenanthrene skeleton at C-2, C-6 and C-7 together with the protons bonded to the aryl rings of **4a**-**h** and **5a**-**g** cause the multiplett at 6.50-7.88 ppm, the signals of the H atom at C-4 (4-H), C-5 (5-H) and C-8 (8-H) are shifted to lower field: 4-H resonates at 8.93 ppm and 5-H at 8.84-8.93 ppm. The signal of 8-H can be found in the spectra of the imines **4a**-**h** at 8.72-8.84 ppm. By replacing the adjacent imino group at C-9 in **4** by the more polarized aldehyde group in **5** it is further shifted downfield to 9.08-9.21 ppm. A characteristic feature of the uv spectra of **4** and **5**, recorded in acetonitrile, is a strong absorption band at 270-274 nm accompanied by another band of lower intensity at longer wavelengths (**4a**-**h**: 328-331 nm, **5a**-**g**: 334-346 nm).

The formation of the transformation products **3** and **4** can be explained by a reaction sequence in which in the first step the 2-methylenedihydroisoquinolines **6**, obtained *in situ* by deprotonation of **2**, are added as carbon nucleophiles of the enamine type at the preferred position 2 of the pyrylium perchlorate **1** [3] to give the 2*H*-pyrans **7**. Then by the well known electrocyclic ring opening of 2*H*-pyrans [17] the merocyanines **8** are formed. One possibility for their stabilization is the cyclization to the betaines **9** followed by protonation and water elimination to the isoquinolinium salts **3** (2,6-[C$_5$+C] ring transformation [18]). A high solvent polarity [19] seems to be necessary for the stabilization of the betaine intermediates **9**. Hence, on replacing the methanol by the less polar ethanol the merocyanines are not cyclized to **9** but undergo an electrocyclic reaction to the spiro derivatives **10** which are related to spiro[cyclohexadiene-indolines] and spiro-[cyclohexadiene-dihydroacridines], the transformation products of the pyrylium salts **1** with methyleneindolines and methylenedihydroacridines, respectively [1,4-7]. An intramolecular amine elimination converts **10** into the benzophenones **11**, the same type of compounds as obtained by the reaction of the salts **1** with methylene-dihydrobenzoxazoles as final products [10]. In the next step the nucleophilic carbon atom of the enamine side chain of **11** attacks the carbonyl group to give the dihydro-phenanthrenes **12**. Water elimination to the phenanthrene aldehyde imines **4** completes the reaction sequence.

Since in the case of the isomeric 3-methyl- and 4-methyl-isoquinolinium salts the deprotonation to a methylene compound is retarded or impossible no reaction occurred.

This novel access to the phenanthrene skeleton combines the transformation of the pyrylium moiety to a benzene ring (2,5-[C$_4$+C$_2$]-transformation [18]) with the ring opening of the nitrogen containing part of the isoquinoline and a ring closure to another benzene ring.
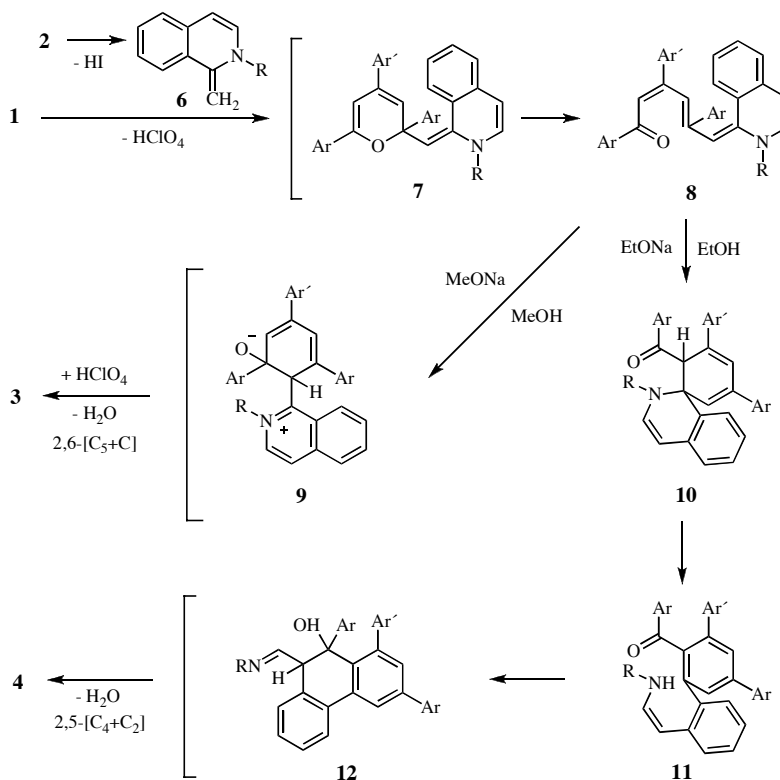
EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ^{1}H nmr and ^{13}C nmr spectra were recorded on a Varian Gemini 200 spectrometer ([1]H: 199.975 MHz, [13]C: 50.289 MHz), on a Varian Gemini 2000 spectrometer ([1]H: 200.041 MHz, [13]C: 50.305 MHz) and on a Varian Gemini 300 spectrometer ([1]H: 300.075 MHz, [13]C: 75.462 MHz) in dimethyl-d_6 sulfoxide (**3**) or in deuteriochloroform (**4**, **5**) at 25 °C (chemical shifts were calibrated to the residual signal of the solvent used [20]), ir spectra were obtained on a Nicolet Thermo Avatar FT-IR 360 spectrophotometer (in potassium bromide) and uv spectra on a Zeiss M 40 instrument (acetonitrile, 25 °C). Mass spectra were determined on a VG ZAB HSQ Analytical Instruments spectrometer (FAB, matrix: 3-nitrobenzyl alcohol) and on a Finnigan MAT 111 A spectrometer (70 eV, electron impact). The pyrylium perchlorates **1a** [21], **1b** [22], **1c** [23], **1d** [24], **1e** [25], **1f,g** [26] and the isoquinolinium iodides **2a,b** [27] were synthesized according to literature procedures.

Synthesis of the 2-Alkyl-1-(2,4,6-triarylphenyl)isoquino-linium Perchlorates 3a-c from the 2,4,6-Triarylpyrylium Perchlorates 1a,b and the 2-alkyl-1-methylisoquinolinium Iodides 2a,b. General Procedure. Sodium metal (0.35 g, 15 mmoles) was dissolved in absolute methanol (30 ml). After addition of 5 mmoles of the pyrylium perchlorate **1** and 5 mmoles of the isoquinolinium iodide **2** the reaction mixture was heated under reflux for two hours. The triarylphenyliso-quinolinium perchlorates **3** crystallized from the hot reaction mixture. They were collected by filtration with suction, washed with water and ethanol and recrystallized from acetonitrile.

2-Methyl-1-(2,4,6-triphenylphenyl)isoquinolinium Perchlorate (3a). This compound was obtained according to the general procedure from **1a** and **2a** in 64% yield, mp 316-317 °C; ^{1}H nmr (DMSO-d_6): δ 4.09 (s, 3H, N[+]CH$_3$), 7.03-8.20 (m, 21H, arom-H), 8.47 (d, 1H, 4-H), 8.60 (d, 1H, 3-H); ms (FAB): m/z 448 [C$_{34}$H$_{26}$N[+]]. *Anal*. Calcd. For C$_{34}$H$_{26}$ClNO$_4$: C, 74.52; H, 4.78; N, 2.56. Found: C, 74.50; H, 4.83; N, 2.40.

Table 3

Crystal Data and Structure Refinement for the *N*-Methyl-[1-(4-methylphenyl)-3,10-diphenylphenanthren-9-ylmethylene]amine (**4b**)

Empirical formula	C$_{35}$H$_{27}$N
Unit cell dimensions	a = 809.8(1) pm α = 71.28(1)°
	b = 1113.7(1) pm β = 79.39(1)°
	c = 1575.6(2) pm γ = 70.85(1)°
Volume	1266.4(3)·10[6] pm[3]
Z	2
Calculated density	1.210 g cm^{-3}
Crystal system	triclinic
Space group	P$\bar{1}$(no. 2)
Diffractometer	STOE IPDS
Temperature	213(2) K
Crystal size	0.90 x 0.22 x 0.09 mm
2θ Range	4° < 2θ < 50°
Reflections	
collected	7777
unique	4270 [R_{int} = 0.030]
reflections with $I > 2\sigma(I)$	2500
Absorption coefficient	μ(Mo-K$_\alpha$) = 0.07 mm^{-1}
Parameters	325

Table 3 (continued)

Refinement method	Full-matrix least-squares on F^2
Programs	SHELX-97
Largest diff. peak and hole	0,26 and –0,25 $e/10^6$ pm^3
$R1$ index, $I>2\sigma(I)$	0.0396
$wR2$ index, all data	0.1073

2-Methyl-1-[4-(4-methylphenyl)-2,6-diphenylphenyl]isoquinolinium Perchlorate (3b). This compound was obtained according to the general procedure from **1a** and **2a** in 56% yield, mp 316-317 °C; ^{1}H nmr (DMSO-d$_6$): δ 2.42 (s, 3H, C$_6$H$_4$C*H$_3$*), 4.13 (s, 3H, N$^+$CH$_3$), 7.06-8.26 (m, 20H, arom-H), 8.52 (d, 1H, 4-H), 8.65 (d, 1H, 3-H); ms (FAB): m/z 462 [C$_{35}$H$_{28}$N$^+$]. *Anal.* Calcd. For C$_{35}$H$_{28}$ClNO$_4$: C, 74.79; H, 5.02; N, 2.49. Found: C, 74.86; H, 5.10; N, 2.38.

2-Ethyl-1-(2,4,6-triphenylphenyl)isoquinolinium Perchlorate (3c). This compound was obtained according to the general procedure from **1a** and **2a** in 63% yield, mp 336-337 °C; ^{1}H nmr (DMSO-d$_6$): δ 0.98 (t, 3H, N$^+$CH$_2$C*H$_3$*), 4.51 (q, 2H, N$^+$C*H$_2$*CH$_3$), 7.01-8.22 (m, 21H, arom-H), 8.52 (d, 1H, 4-H), 8.71 (d, 1H, 3-H); ms (FAB): m/z 462 [C$_{35}$H$_{28}$N$^+$]. *Anal.* Calcd. For C$_{35}$H$_{28}$ClNO$_4$: C, 74.79; H, 5.02; N, 2.49. Found: C, 74.72; H, 4.98; N, 2.37.

Preparation of the *N*-Alkyl-(1,3,10-triarylphenanthren-9-ylmethylene)amines 4a-h from the 2,4,6-Triarylpyrylium Perchlorates 1a-g and the 2-Alkyl-1-methylisoquinolinium Iodides 2a,b. General Procedure (*cf.* Tables 1 and 2). To a solution of sodium ethanolate in ethanol, prepared by dissolving sodium metal (0.35 g, 15 mmoles) in 30 ml of absolute ethanol, 5 mmoles of the pyrylium perchlorate **1** and 5 mmoles of the isoquinolinium iodide **2** were added. The reaction mixture was then refluxed for two hours. The imines **4** crystallized in the most cases from the hot reaction mixture. Otherwise their crystallization was initiated by cooling. The products were collected by filtration with suction, washed with water and ethanol and recrystallized from ethanol/toluene.

Hydrolysis of the *N*-Alkyl-(1,3,10-triarylphenanthren-9-ylmethylene)amines 4a-h to the 1,3,10-Triarylphenanthrene-9-carbaldehydes 5a-g. General Procedure (*cf.* Tables 1 and 2). 1.5 mmoles of the amine **4**, 10 ml of water, 10 ml of concentrated hydrochloric acid and 40 ml of ethanol were refluxed for 30 minutes. After cooling the aldehydes **5** were collected by filtration with suction, washed with water and ethanol and recrystallized from ethanol/toluene.

X-Ray Structure Determination (*cf.* Table 3). Appropriate crystals of the phenanthrene aldehyde imine **4b** were obtained by slow cooling of an ethanol/toluene solution.

The data collection for the X-ray structure determination of **4b** was carried out on a diffractometer STOE IPDS using Mo-K$_\alpha$ radiation (λ = 71.073 pm, graphite-monochromator). The hydrogen atom positions were calculated for idealised positions. The programs SHELX-97 [28] and DIAMOND2 [29] were used.

More details on data collection and structure determination are summarized in Table 3. Further details have been deposited with the Cambridge Crystallographic Data Centre as CCDC 618727.

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