Ring Transformations of Heterocyclic Compounds. **XXII** [1]. Pyrido[1,2-*a*]indolium Salts from 2-Methyl-3*H*-indoles by Pyrylium Mediated Three Carbon Annelation

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The synthesis of pyrido[1,2-*a*]indolium perchlorates **8**,**11** from 2,4,6-triarylpyrylium perchlorates **1** and 2-methyl-3*H*-indoles **6**,**9** in the presence of a basic condensing agent (anhydrous sodium acetate, piperidine acetate, triethylamine/acetic acid, triethylamine) in ethanol by a 2,4-[C_3+C_2N] pyrylium ring transformation is reported. Spectroscopic data of the transformation products and their mode of formation are discussed.

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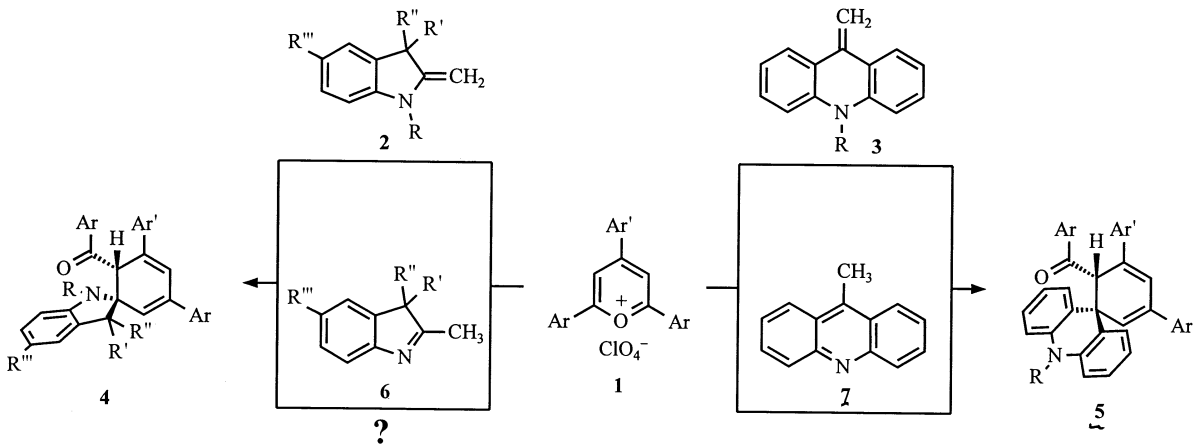
Some years ago it was found that 2,4,6-triarylpyrylium salts **1** [2] react with 2-methyleneindolines **2** (R = Me, Ph; R'= R"= Me) [3] by a diastereoselective ring transformation to give the aroylspiro[cyclohexadiene-indolines] **4** [4,5], which represent first examples of a new class of photochromic compounds, the aroylspiro[cyclohexadiene-azaheterocycles] [6]. The transformation was later extended to 2-methyleneindolines **2** with two different substituents or a spiro-fused carbocycle/heterocycle at C-3 [7,1] as well as to their benzo-fused analogues [8].

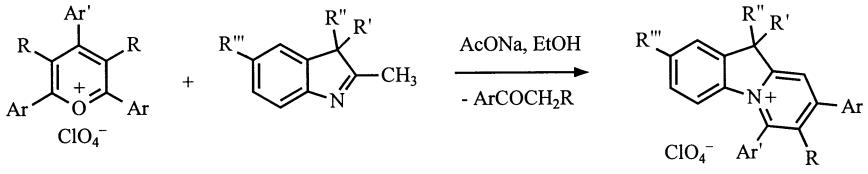
Acridine derivatives were found to be further candidates for the synthesis of spiro compounds [9]. The transformation of the salts **1** with 9-methylenedihydroacridines **3** led to aroylspiro[cyclohexadiene-dihydroacridines] **5** [4] also showing interesting photochromic properties [10]. Since 9-methylacridine (**7**) reacted to give the *N*-unsubstituted spirodihydroacridines **5** (R = H), the idea arose to study transformations of the pyrylium salts **1** with the structurally related 3*H*-indoles **6** with the aim to synthesize spiroindolines **4** of the secondary amine type (R = H), which would offer possibilities for further manipulations at the nitrogen atom. Surprisingly, the reactions proceeded quite differently. In this paper we wish to report on these investigations.

When the 2,4,6-triarylpyrylium perchlorates **1a-h** and the 3,3-dimethyl substituted 3*H*-indoles **6a-h** were refluxed in ethanol in the presence of anhydrous sodium acetate, instead of the expected spiro compounds of the type **4**, the pyrido[1,2-*a*]indolium perchlorates **8a-o** were obtained. In the same manner the 3*H*-indoles **6i-k** with different substituents or a spiro-fused carbocycle at C-3 gave rise to the indolium perchlorates **8p-r**. The example **1i** + **6a** → **8s** shows that the transformation can be extended to 3,5-disubstituted 2,4,6-triarylpyrylium salts. In the case of benzo-fused 3*H*-indoles the success of the transformations strongly depends on the position of the additional benzene ring. Whereas the benzo[*e*]indole **9** reacted smoothly with the pyrylium salt **1a** to give the benzo[*e*]pyrido[1,2-*a*]indolium perchlorate **11**, no pyridinium salt **12** could be obtained starting with the benzo[*g*]isomer **10**. Obviously, a strong steric interaction between the α-bonded phenyl substituent and the fused benzene ring in **12**, which is not present in **11**, prevents its formation. In all the transformations the sodium acetate, used as basic condensing agent, can be successfully substituted by piperidine acetate or triethylamine/acetic acid, whereas triethylamine itself diminishes the yield and sodium ethanolate is totally ineffective (*cf.* experimental part).



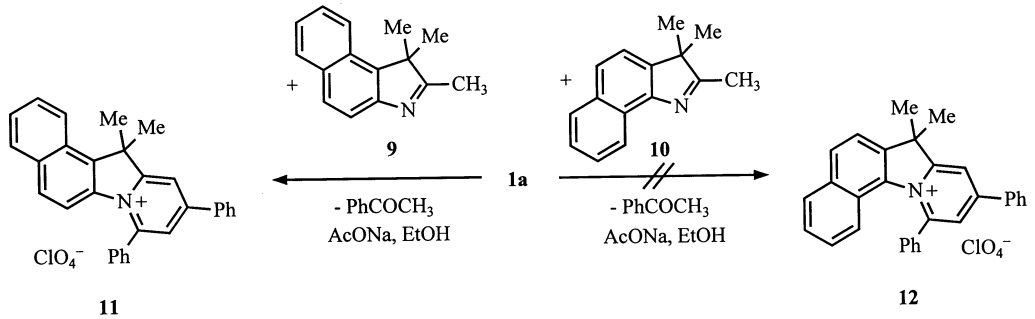
Pyrido[1,2-*a*]indolium salts of the type **8** have been reported in the patent literature to be optical whiteners [11]. In comparison to the only other known method for their preparation, the reaction of 3*H*-indoles with α,β-unsaturated ketones in the presence of strong acids [12], their synthesis *via* pyrylium ring transformation proceeds under milder conditions, with shorter reaction times and with higher yields.

Concerning the mechanism of the transformations one may assume that the 3*H*-indole **6** attacks the pyrylium cation of **1** in the primary step at the preferred position 2



1 **6** **8**

1	**6**	Ar	Ar'	R	R'	R''	R'''	**8**
a	**a**	Ph	Ph	H	Me	Me	H	**a**
b	**a**	Ph	4-Me-C_6H_4	H	Me	Me	H	**b**
c	**a**	Ph	4-MeO-C_6H_4	H	Me	Me	H	**c**
d	**a**	Ph	4-Cl-C_6H_4	H	Me	Me	H	**d**
e	**a**	Ph	4-Br-C_6H_4	H	Me	Me	H	**e**
f	**a**	4-Me-C_6H_4	Ph	H	Me	Me	H	**f**
g	**a**	4-Cl-C_6H_4	Ph	H	Me	Me	H	**g**
h	**a**	4-Br-C_6H_4	Ph	H	Me	Me	H	**h**
a	**b**	Ph	Ph	H	Me	Me	Me	**i**
a	**c**	Ph	Ph	H	Me	Me	MeO	**j**
a	**d**	Ph	Ph	H	Me	Me	*t*-Bu	**k**
a	**e**	Ph	Ph	H	Me	Me	F	**l**
a	**f**	Ph	Ph	H	Me	Me	Cl	**m**
a	**g**	Ph	Ph	H	Me	Me	Br	**n**
a	**h**	Ph	Ph	H	Me	Me	I	**o**
a	**i**	Ph	Ph	H	Me	Et	H	**p**
a	**j**	Ph	Ph	H	Me	CH_2Ph	H	**q**
a	**k**	Ph	Ph	H	$(CH_2)_5$		H	**r**
i	**a**	Ph	Ph	Me	Me	Me	H	**s**

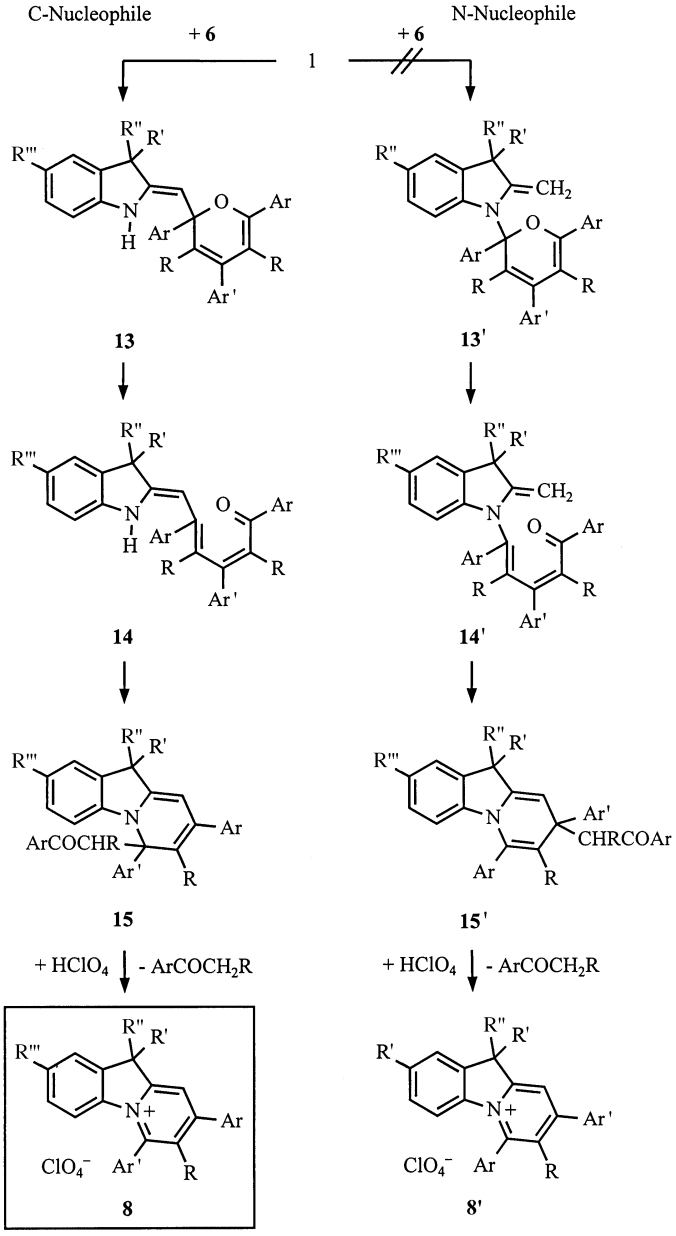


11 **9** **1a** **10** **12**

[2] as a carbon nucleophile with the C-atom of the 2-positioned methyl group or as a nitrogen nucleophile with its N-atom. In the first case the 2*H*-pyran intermediate **13** [13] would be formed, from which after electrocyclic ring opening to **14**, recyclization to **15** and perchloric acid assisted alkylarylketone elimination the pyrido[1,2-*a*]-indolium perchlorates **8**' are obtained. As shown for the transformation **1a** + **6a** → **8a**, the ketone by-product can be isolated from the reaction mixture as a 2,4-dinitrophenylhydrazone derivative. Since in the course of this transformation a pyridinium moiety is built up from three carbon atoms of the pyrylium cation and a C_2N-fragment of the 3*H*-indole, which connects the former positions 2 and 4 of **1**, the reaction can be classified as a 2,4-[C_3+C_2N] ring transformation [14].

If the 3*H*-indole **6** acts as an nitrogen nucleophile *via* the intermediates **13**', **14**' and **15**' the isomeric pyrido[1,2-*a*]-indolium perchlorates **8**', as the result of a 2,4-[C_3+NC_2] ring transformation [14], would be formed. Because the reaction of the pyrylium salts **1a** and **1i** leads to the same products according to both mechanisms, a decision between the mechanistic alternatives cannot be made. The transformations of the salts **1b-h** give only indolium salts of

the type **8**, clearly indicating that the 3*H*-indole **6** attacks the pyrylium cation with carbon in the primary step.



The elemental analyses and the spectroscopic data (*cf.* Tables 1 and 2) strongly support the structure proposed for the pyrido[1,2-*a*]indolium perchlorates **8**,**11**. In the ^{1}H nmr spectra the methyl groups at C-10 of **8** and C-12 of **11** show the expected singlet at 1.72-2.06 ppm. The multiplet at 6.49-8.50 ppm can be attributed to protons of the benzene ring(s) of the indolium moiety and the two aryl substituents. The signal of the proton at C-4 of **8** and C-6 of **11** is remarkably shifted to higher field by the anisotropy effect of the aryl ring at C-6 of **8** and C-8 of **11**, respectively. This is caused by the almost perpendicular orientation of the aryl ring to the molecular plane due to its steric interaction with the indolium system. This signal can be located at 5.78-6.42 ppm, split into a doublet by coupling with the *ortho*-bonded proton with a characteristic coupling constant of 5.7-9.4 Hz [15]. NOe experiments have shown that in the case of the pyrido[1,2-*a*]indolium perchlorates **8b-h** the aryl substituent Ar' and not Ar is found adjacent to the proton at C-4, thus ruling out the alternative structures **8'b-h**. By the same type of experiment, it was found that the doublet at 8.91-9.11 ppm corresponds to a proton in the neighbourhood of a methyl group at C-10 of **8** and C-12 of **11**. Hence, this signal has to be attributed to the H-atom in position 9 of **8** (position 11 of **11**) and the doublet at 8.32-8.43 ppm to the remaining proton of the pyridinium ring. The coupling constant of 1.1-2.0 Hz determined for both doublets is comparable to those observed for protons in 3,5-position of other pyridinium derivatives [16].

A characteristic feature of the uv-spectra is a strong absorption band at 329-356 nm [17]. FAB mass spectra, recorded for **8a**, **8b** and **8f**, show exactly the mass peaks of the corresponding cations.

Further support for the structure of the pyrido[1,2-*a*]-indolium perchlorates **8**,**11** was obtained by an independent synthesis of **8a** and **8c**. According to a modified literature procedure, 1,3-diphenylpropen-1-one and 1-(4-methoxyphenyl)-3-phenylpropen-1-one, respectively, were treated with 2,3,3-trimethyl-3*H*-indolium perchlorate. The pyrido[1,2-*a*]indolium perchlorates **8a** and **8c** obtained were identical in all respects with those synthesized by ring transformation of the pyrylium salts **1a**,**1c** with the 3*H*-indole **6a**.

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) and on a Varian Gemini 2000 spectrometer (^{1}H: 200.041 MHz, ^{13}C: 50.305 MHz) in deuteriochloroform or dimethyl-d_6 sulfoxide at 25° with hexamethyl disiloxane as internal standard and uv spectra on a Zeiss M 40 instrument (acetonitrile, 25°). Mass spectra were determined on a VG ZAB HSQ Analytical Instruments spectrometer (FAB, matrix: 3-nitrobenzyl alcohol). The pyrylium perchlorates **1a** [18], **1b** [19], **1c** [20], **1d** [21], **1e** [22], **1f-h** [23], **1i** [24], 1-naphthylhydrazine [25], 3-methyl-4-phenylbutan-2-one [26] and 1-(4-methoxyphenyl)-3-phenylpropen-1-one [27] were synthesized according to literature procedures. The 2,3,3-trimethyl-3*H*-indol, phenylhydrazine, 4-methylphenylhydrazine hydrochloride, 4-fluorophenylhydrazine hydrochloride, 4-chlorophenylhydrazine hydrochloride, 4-bromophenylhydrazine hydrochloride, 3-methylbutan-2-one, 3-methylpentan-2-one and 1,3-diphenylpropen-1-one were purchased from Aldrich, 4-methoxyphenylhydrazine hydrochloride and 1,1,2-trimethyl-1*H*-benzo[*e*]-indole from Acros, 4-*tert*-butylphenylhydrazine hydrochloride as well as 4-iodophenylhydrazine from Lancaster and 1-cyclhexylethanone from Fluka.

Table 1
Physical and Analytical Data for the Pyrido[1,2-*a*]indolium Perchlorates **8**,**11**

No.	perchlorate	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N
8a	10,10-Dimethyl-6,8-diphenyl-10*H*-pyrido[1,2-*a*]-indolium	49	331-332	$C_{26}H_{22}ClNO_4$ (447.9)	69.72 69.70	4.95 4.93	3.13 3.16
8b	10,10-Dimethyl-6-(4-methylphenyl)-8-phenyl-10*H*-pyrido[1,2-*a*]indolium	58	280-281	$C_{27}H_{24}ClNO_4$ (461.9)	70.20 70.32	5.24 5.30	3.03 3.03
8c	6-(4-Methoxyphenyl)-10,10-dimethyl-8-phenyl-10*H*-pyrido[1,2-*a*]indolium	68	259-260	$C_{27}H_{24}ClNO_5$ (477.9)	67.85 67.80	5.06 5.20	2.93 2.88
8d	6-(4-Chlorophenyl)-10,10-dimethyl-8-phenyl-10*H*-pyrido[1,2-*a*]indolium	46	283-284	$C_{26}H_{21}Cl_2NO_4$ (482.4)	64.74 64.86	4.39 4.30	2.90 2.95
8e	6-(4-Bromophenyl)-10,10-dimethyl-8-phenyl-10*H*-pyrido[1,2-*a*]indolium	52	265-266	$C_{26}H_{21}BrClNO_4$ (526.8)	59.28 59.10	4.02 4.10	2.66 2.73
8f	10,10-Dimethyl-8-(4-methylphenyl)-6-phenyl-10*H*-pyrido[1,2-*a*]indolium	55	314-315	$C_{27}H_{24}ClNO_4$ (461.9)	70.20 70.20	5.24 5.26	3.03 3.15
8g	8-(4-Chlorophenyl)-10,10-dimethyl-6-phenyl-10*H*-pyrido[1,2-*a*]indolium	74	297-298	$C_{26}H_{21}Cl_2NO_4$ (482.4)	64.74 64.68	4.39 4.45	2.90 2.96
8h	8-(4-Bromophenyl)-10,10-dimethyl-6-phenyl-10*H*-pyrido[1,2-*a*]indolium	34	289-290	$C_{26}H_{21}BrClNO_4$ (526.8)	59.28 59.20	4.02 4.00	2.66 2.70
8i	2,10,10-Trimethyl-6,8-diphenyl-10*H*-pyrido-[1,2-*a*]indolium	31	306-307	$C_{27}H_{24}ClNO_4$ (461.9)	70.20 70.30	5.24 5.24	3.03 3.10
8j	2-Methoxy-10,10-dimethyl-6,8-diphenyl-10*H*-pyrido[1,2-*a*]indolium	51	232-233	$C_{27}H_{24}ClNO_5$ (477.9)	67.85 67.81	5.06 5.18	2.93 2.88
8k	2-tert-Butyl-10,10-dimethyl-6,8-diphenyl-10*H*-pyrido[1,2-*a*]indolium	47	275-276	$C_{30}H_{30}ClNO_4$ (504.0)	71.49 71.55	6.00 6.12	2.78 2.83
8l	2-Fluoro-10,10-dimethyl-6,8-diphenyl-10*H*-pyrido[1,2-*a*]indolium	32	295-296	$C_{26}H_{21}ClFNO_4$ (465.9)	67.03 67.20	4.54 4.60	3.01 3.03
8m	2-Chloro-10,10-dimethyl-6,8-diphenyl-10*H*-pyrido[1,2-*a*]indolium	35	306-307	$C_{26}H_{21}Cl_2NO_4$ (482.4)	64.74 64.70	4.39 4.45	2.90 2.86
8n	2-Bromo-10,10-dimethyl-6,8-diphenyl-10*H*-pyrido[1,2-*a*]indolium	42	296-297	$C_{26}H_{21}BrClNO_4$ (526.8)	59.28 59.36	4.02 4.10	2.66 2.73
8o	2-Iodo-10,10-dimethyl-6,8-diphenyl-10*H*-pyrido[1,2-*a*]indolium	23	286-287	$C_{26}H_{21}ClINO_4$ (573.8)	54.42 54.20	3.69 3.75	2.44 2.38
8p	10-Ethyl-10-methyl-6,8-diphenyl-10*H*-pyrido-[1.2-*a*]indolium	36	231-232	$C_{27}H_{24}ClNO_4$ (461.9)	70.20 70.10	5.24 5.30	3.03 2.98
8q	10-Benzyl-10-methyl-6,8-diphenyl-10*H*-pyrido-[1,2-*a*]indolium	30	296-297	$C_{32}H_{26}ClNO_4$ (524.0)	73.35 73.40	5.00 5.10	2.67 2.73
8r	6′,8′-Diphenyl-10′*H*-spiro[cyclohexane-1,10′-pyrido[1,2-*a*]indolium]	43	287-288	$C_{29}H_{26}ClNO_4$ (488.0)	71.38 71.40	5.37 5.43	2.87 2.95
8s	7,10,10-Trimethyl-6,8-diphenyl-10*H*-pyrido-[1,2-*a*]indolium	17 [a]	312-313	$C_{27}H_{24}ClNO_4$ (461.9)	70.20 70.31	5.24 5.18	3.03 3.18
11	12,12-Dimethyl-8,10-diphenyl-12*H*-benzo[e]-pyrido[1,2-*a*]indolium	51	290-291	$C_{30}H_{24}ClNO_4$ (498.0)	72.36 72.40	4.86 4.80	2.81 2.90

[a] Reaction time: 24 h.

Preparation of the 3*H*-Indoles **6** and **10.**

The 3*H*-indoles **6b-k** and **10** were synthesized by Fischer indolization [28] from *N*-arylhydrazines or their hydrochlorides and α-branched ketones in the presence of perchloric acid in boiling ethanol as previously reported [1]. The resulting oily crude products were used without further purification. Their identity was checked by nmr spectroscopy and in the case of known compounds the data were compared with reported values.

2,3,3,5-Tetramethyl-3*H*-indole (**6b**) [29].

This compound was obtained from 4-methylphenylhydrazine hydrochloride and 3-methylbutan-2-one in 89% yield; ^{1}H nmr (deuteriochloroform): δ 1.20 (s, 6H, 3,3-$(CH_3)_2$), 2.17 (s, 3H, 5-CH_3), 2.31 (s, 3H, 2-CH_3), 7.00-7.30 (m, 3H, arom-H).

5-Methoxy-2,3,3-trimethyl-3*H*-indol (**6c**) [30].

This compound was obtained from 4-methoxyphenylhydrazine hydrochloride and 3-methylbutan-2-one in 95% yield; ^{1}H nmr (deuteriochloroform): δ 1.21 (s, 6H, 3,3-$(CH_3)_2$), 2.17 (s, 3H, 2-CH_3), 3.75 (s, 3H, 5-OCH_3), 6.73-7.38 (m, 3H, arom-H).

5-*tert*-Butyl-2,3,3-trimethyl-3*H*-indole (**6d**).

This compound was obtained from 4-*tert*-butylphenylhydrazine hydrochloride and 3-methylbutan-2-one in 96% yield; ^{1}H nmr (deuteriochloroform): δ 1.21 (s, 6H, 3,3-$(CH_3)_2$), 1.27 (s, 9H, 5-$C(CH_3)_3$), 2.18 (s, 3H, 2-CH_3), 7.20-7.41 (m, 3H, arom-H).

5-Fluoro-2,3,3-trimethyl-3*H*-indole (**6e**) [31].

This compound was obtained from 4-fluorophenylhydrazine hydrochloride and 3-methylbutan-2-one in 88% yield; ^{1}H nmr

Table 2

Spectral Data for the Pyrido[1,2-*a*]indolium Perchlorates **8**,**11**

Compound	UV (CH_3CN) λ_{max} (nm) (log ε)	^{1}H-NMR (dimethyl-d_6 sulfoxide) [a] δ (ppm)
8a [b]	227 sh (4.19), 329 (4.53)	1.80 (s, 6H, 10,10-$(CH_3)_2$), 6.21 (d, J = 8.4 Hz, 1H, 4-H), 7.17-8.38 (m, 13H, arom-H), 8.38 (d, J = 1.9 Hz, 1H, 7-H), 8.97 (d, J = 1.9 Hz, 1H, 9-H)
8b [b]	228 sh (4.17), 330 (4.52)	1.79 (s, 6H, 10,10-$(CH_3)_2$), 2.47 (s, 3H, 6-C*H*$_3$C$_6$H$_4$), 6.35 (d, J = 8.4 Hz, 1H, 4-H), 7.19-8.27 (m, 12H, arom-H), 8.32 (d, J = 1.9 Hz, 1H, 7-H), 8.94 (d, J = 1.9 Hz, 1H, 9-H)
8c	228 sh (4.28), 331 (4.54)	1.78 (s, 6H, 10,10-$(CH_3)_2$), 3.89 (s, 3H, 6-C*H*$_3$OC$_6$H$_4$), 6.42 (d, J = 8.4 Hz, 1H, 4-H), 7.23-8.26 (m, 12H, arom-H), 8.32 (d, J = 1.8 Hz, 1H, 7-H), 8.92 (d, J = 1.8 Hz, 1H, 9-H)
8d	228 sh (4.28), 330 (4.55)	1.78 (s, 6H, 10,10-$(CH_3)_2$), 6.37 (d, J = 8.4 Hz, 1H, 4-H), 7.25-8.27 (m, 12H, arom-H), 8.38 (d, J = 1.7 Hz, 1H, 7-H), 8.97 (d, J = 1.7 Hz, 1H, 9-H)
8e	229 (4.29), 331 (4.51)	1.78 (s, 6H, 10,10-$(CH_3)_2$), 6.39 (d, J = 8.4 Hz, 1H, 4-H), 7.33-8.26 (m, 12H, arom-H), 8.38 (d, J = 1.8 Hz, 1H, 7-H), 8.97 (d, J = 1.8 Hz, 1H, 9-H)
8f [b]	230 (4.18), 341 (4.57)	1.79 (s, 6H, 10,10-$(CH_3)_2$), 2.38 (s, 3H, 8-C*H*$_3$C$_6$H$_4$), 6.19 (d, J = 8.4 Hz, 1H, 4-H), 7.16-8.23 (m, 12H, arom-H), 8.35 (d, J = 1.8 Hz, 1H, 7-H), 8.95 (d, 1.8 Hz, 1H, 9-H)
8g	229 (4.21), 334 (4.55)	1.79 (s, 6H, 10,10-$(CH_3)_2$), 6.22 (d, J = 8.4 Hz, 1H, 4-H), 7.17-8.33 (m, 12H, arom-H), 8.41 (d, J = 1.8 Hz, 1H, 7-H), 8.98 (d, J = 1.8 Hz, 1H, 9-H)
8h	229 sh (4.21), 336 (4.57)	1.78 (s, 6H, 10,10-$(CH_3)_2$), 6.21 (d, J = 8.4 Hz, 1H, 4-H), 7.17-8.25 (m, 12H, arom-H), 8.42 (d, J = 2.0 Hz, 1H, 7-H), 8.99 (d, J = 2.0 Hz, 1H, 9-H)
8i	229 (4.20), 336 (4.50)	1.78 (s, 6H, 10,10-$(CH_3)_2$), 2.32 (s, 3H, 2-CH_3), 6.08 (d, J = 8.5 Hz, 1H, 4-H), 6.98-8.26 (m, 12H, arom-H), 8.35 (d, J = 1.4 Hz, 1H, 7-H), 8.94 (d, J = 1.4 Hz, 1H, 9-H)
8j	229 sh (4.13), 297 (4.07), 356 (4.39)	1.78 (s, 6H, 10,10-$(CH_3)_2$), 3.77 (s, 3H, 2-CH_3O), 6.08 (d, J = 9.2 Hz, 1H, 4-H), 6.74-8.25 (m, 12H, arom-H), 8.33 (d, J = 1.7 Hz, 1H, 7-H), 8.91 (d, J = 1.7 Hz, 1H, 9-H)
8k	229 sh (4.19), 337 (4.51)	124 (s, 9H, 2-C$(CH_3)_3$), 1.79 (s, 6H, 10,10-$(CH_3)_2$), 6.10 (d, J = 9.2 Hz, 1H, 4-H), 7.21-8.28 (m, 12H, arom-H), 8.36 (d, J = 1.8 Hz, 1H, 7-H), 8.94 (d, J = 1.8 Hz, 1H, 9-H)
8l	228 (4.21), 330 (4.51)	1.80 (s, 6H, 10,10-$(CH_3)_2$), 6.21 (m, 1H, 4-H), 7.09-8.26 (m, 12H, arom-H), 8.38 (d, J = 1.1 Hz, 1H, 7-H), 8.96 (d, J = 1.1 Hz, 1H, 9-H)
8m	229 sh (4.28), 333 (4.56)	1.79 (s, 6H, 10,10-$(CH_3)_2$), 6.17 (d, J = 9.3 Hz, 1H, 4-H), 7.32-8.28 (m, 12H, arom-H), 8.40 (d, J = 2.0 Hz, 1H, 7-H), 8.96 (d, J = 2.0 Hz, 1H, 9-H)
8n	229 sh (4.27), 336 (4.57)	1.81 (s, 6H, 10,10-$(CH_3)_2$), 6.13 (d, J = 8.8 Hz, 1H, 4-H), 7.42-8.28 (m, 12H, arom-H), 8.37 (d, J = 1.8 Hz 1H, 7-H), 8.95 (d, J = 1.8 Hz 1H, 9-H)
8o	231 sh (4.31), 309 sh (4.33), 341 (4.58)	1.77 (s, 6H, 10,10-$(CH_3)_2$), 5.96 (d, J = 8.8 Hz, 1H, 4-H), 7.57-8.36 (m, 12H, arom-H), 8.37 (d, J = 2.0 Hz, 1H, 7-H), 8.94 (d, J = 2.0 Hz, 1H, 9-H)
8p	228 sh (4.21), 331 (4.50)	0.43 (t, 3H, 10-CH_2CH_3), 1.82 (s, 3H, 10-CH_3), 2.41 (m, 2H, 10-CH_2CH_3), 6.26 (d, J = 8.4 Hz, 1H, 4-H), 7.19-8.31 (m, 13H, arom-H), 8.42 (d, J = 1.9 Hz, 1H, 7-H), 8.94 (d, J = 1.9 Hz, 1H, 9-H)
8q	228 sh (4.23), 333 (4.49)	1.96 (s, 3H, 10-CH_3), 3.52 (d, J = 12.9 Hz, 1H, 3-CH_2Ph), 3.75 (d, J = 12.9 Hz, 1H, 3-CH_2Ph), 5.98 (d, J = 8.4 Hz, 1H, 4-H), 6.48-8.32 (m, 18H, arom-H), 8.35 (d, J = 1.5 Hz, 1H, 7-H), 9.09 (d, J = 1.5 Hz, 1H, 9-H)
8r	228 sh (4.23), 329 (4.53)	1.77-2.42 (m, 10H, 10',10'-$(CH_2)_5$), 6.31 (d, J = 5.7 Hz, 1H, 4'-H), 7.21-8.28 (m, 13H, arom-H), 8.35 (d, J = 1.1 Hz, 1H, 7'-H), 8.94 (d, J = 1.1 Hz, 1H, 9'-H)
8s	229 sh (4.26), 309 (4.38)	1.72 (s, 6H, 10-$(CH_3)_2$), 2.07 (s, 3H, 7-CH_3), 5.78 (d, J = 8.4 Hz, 1H, 4-H), 7.12-7.87 (m, 13H, arom-H), 8.58 (s, 1H, 9-H)
11	254 sh (4.21), 298 (4.46), 333 (4.46), 369 (4.24)	2.06 (s, 6H, 12,12-$(CH_3)_2$), 6.41 (d, J = 9.4 Hz, 1H, 6-H), 7.63-8.50 (m, 15H, arom-H), 8.43 (d, J = 1.8 Hz, 1H, 9-H), 9.11 (d, J = 1.8 Hz, 1H, 11-H)

[a] 4-H, 4'-H, 7-H, 7'-H, 9H and 9'-H denote the protons in 4-, 4'-, 7-, 7'-, 9- and 9'-position of **8**, 6-H, 9-H and 11-H those in 6-, 9- and 11-position of **11** and arom-H the other protons bonded to the benzene rings. [b] Mass spectra (FAB): m/z **8a** 348 [$C_{26}H_{22}N^+$], **8b** 362 [$C_{27}H_{24}N^+$], **8f** 362 [$C_{27}H_{24}N^+$].

(deuteriochloroform): δ 1.21 (s, 6H, 3,3-$(CH_3)_2$), 2.19 (s, 3H, 2-CH_3), 6.85-7.42 (m, 3H, arom-H).

5-Chloro-2,3,3-trimethyl-3*H*-indole (**6f**) [32].

This compound was obtained from 4-chlorophenylhydrazine hydrochloride and 3-methylbutan-2-one in 88% yield; ^{1}H nmr (deuteriochloroform): δ 1.22 (s, 6H, 3,3-$(CH_3)_2$), 2.20 (s, 3H, 2-CH_3), 7.17-7.39 (m, 3H, arom-H).

5-Bromo-2,3,3-trimethyl-3*H*-indole (**6g**) [31].

This compound was obtained from 4-bromophenylhydrazine hydrochloride and 3-methylbutan-2-one in 98% yield; ^{1}H nmr (deuteriochloroform): δ 1.18 (s, 6H, 3,3-$(CH_3)_2$), 2.16 (s, 3H, 2-CH_3), 7.30 (s, 3H, arom-H).

5-Iodo-2,3,3-trimethyl-3*H*-indole (**6h**) [31].

This compound was obtained from 4-iodophenylhydrazine and 3-methylbutan-2-one in 94% yield; ^{1}H nmr (deuteriochloroform) δ 1.22 (s, 6H, 3,3-$(CH_3)_2$), 2.19 (s, 3H, 2-CH_3), 7.21-7.56 (m, 3H, arom-H).

3-Ethyl-2,3-dimethyl-3*H*-indole (**6i**) [33].

This compound was obtained from phenylhydrazine and 3-methyl-4-phenylbutan-2-one in 84% yield; ^{1}H nmr (deuteriochloroform): δ 0.33 (t, 3H, 3-CH_2CH_3), 1.21 (s, 3H, 3-CH_3), 1.78 (m, 2H, 3-CH_2CH_3), 2.17 (s, 3H, 2-CH_3), 7.11-7.48 (m, 4H, arom-H).

3-Benzyl-2,3-dimethyl-3*H*-indole (**6j**) [34].

This compound was obtained from phenylhydrazine and 3-methyl-4-phenylbutan-2-one in 82% yield; ^{1}H nmr (deuteriochloroform): δ 1.30 (s, 3H, 3-CH_3), 2.26 (s, 3H, 2-CH_3), 2.76 (d, J = 13.5 Hz, 1H, 3-CH_2Ph), 3.10 (d, J = 13.5 Hz, 1H, 3-CH_2Ph), 6.71-7.38 (m, 9H, arom-H).

2'-Methylspiro[cyclohexane-1,3'-indol] (**6k**) [35].

This compound was obtained from phenylhydrazine and 1-cyclohexylethanone in 98% yield; ^{1}H nmr (deuteriochloroform): δ 1.18-1.91 (m, 10H, 3',3'-$(CH_2)_5$), 2.23 (s, 3H, 2'-CH_3), 6.95-7.66 (m, 4H, arom-H).

2,3,3-Trimethyl-3*H*-benzo[g]indole (**10**) [32].

This compound was obtained from 1-naphthylhydrazine and 3-methylbutan-2-one in 98% yield; ^{1}H nmr (deuteriochloroform): δ 1.25 (s, 6H, 3-CH_3), 2.30 (s, 3H, 2-CH_3), 7.32-8.52 (m, 6H, arom-H).

Synthesis of Pyrido[1,2-*a*]indolium Perchlorates **8**,**11** from 2,4,6-Triarylpyrylium Perchlorates **1** and 2-Methyl-3*H*-indoles **6**,**10**.

General Procedure (*cf.* Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate **1**, 5 mmoles 3*H*-indole **6**,**10** and anhydrous sodium acetate (0.82 g, 10 mmoles) were added. The reaction mixture was then refluxed, if not otherwise stated, for two hours. The pyrido[1,2-*a*]indolium perchlorates **6**,**11** crystallized from the hot reaction mixture or crystallization was initiated by cooling. The salts were filtered by suction, washed with ethanol, water (to remove sodium salts), again with ethanol, finally with ether and recrystallized from ethanol/acetonitrile.

If the pyrylium salt **1a** was reacted with the 3*H*-indole **10** no pyrido[1,2-*a*]indolium perchlorate **12** could be isolated.

Determination of the Influence of the Condensing Agent Used on the Product Yield.

To study how various condensing agents influence the product yield, the transformation **1a** + **6a** → **8a** was performed instead in the presence of sodium acetate with equimolar amounts of the following agents (yield of **8a** in parenthesis): piperidine acetate (33%), triethylamine/acetic acid (48%), triethylamine (14%), sodium ethanolate (0%).

Isolation of the Alkylarylketone Formed as By-product.

The transformation **1a** + **6a** → **8a** was carried out according to the general procedure. After isolation of **8a** by filtration the mother liquor obtained was poured into a solution of 2,4-dinitrophenylhydrazine (0.99 g, 5 mmole) in 5 ml of concentrated sulfuric acid, 7.5 ml of water and 25 ml of ethanol under magnetic stirring. The acetophenone-2,4-dinitrophenylhydrazone precipitated was filtered by suction, washed with water and ethanol and dried *in vacuo* over phosphorous pentoxide, yield 65%, mp 247-248° (ethylacetate), lit mp 248° [36].

Independent Synthesis of the Pyrido[1,2-*a*]indolium Perchlorates **8a** and **8c**.

The pyrido[1,2-*a*]indolium perchlorates **8a** and **8c** were synthesized applying a modified literature procedure [12]. To 1,3-diphenylpropen-1-one (1.04 g, 5 mmoles) and 1-(4-methoxyphenyl)-3-phenylpropen-1-one, respectively, were added 1.30 g (5 mmoles) 2,3,3-trimethyl-3*H*-indolium perchlorate, prepared by dropping an equimolar amount of perchloric acid (70% in water) to an etheral solution of 2,3,3-trimethyl-3*H*-indol and filtration of the crystalline product. After magnetically stirring the reaction mixture for 5 hours at 120° (oil bath), addition of 10 ml of absolute ethanol, refluxing for 10 minutes and cooling to room temperature, the precipitate was filtered by suction and washed with ethanol and ether to give 0.45 g (20%) of 10,10-dimethyl-6,8-diphenyl-10*H*-pyrido[1,2-*a*]indolium perchlorate (**8a**), mp 331-332° (lit yield 30%, mp >310°) and 0.62 g (26%) of 6-(4-methoxyphenyl)-10,10-dimethyl-8-phenyl-10*H*-pyrido[1,2-*a*]indolium perchlorate (**8c**), mp 259-260° (lit yield 43%, mp 245°), respectively. Both compounds were identical in all respects with those obtained from the pyrylium salts **1a**,**1c** and the 3*H*-indole **6a**.

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