Diastereoselective Built-up of an Aroylcyclohexadiene Moiety as Second Spiro-connected Ring at Spiroindolines by Pyrylium Ring Transformation

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2,4,6-Triarylpyrylium perchlorates **1** react with methyleneindolines **3** *in situ* generated from the corresponding methylindolium salts **2**, which are spiro-fused with a cycloalkane, benzanellated cycloalkene or a heterocyclic system. These diastereoselective 2,5-[C$_4$+C$_2$] pyrylium ring transformations are carried out in the presence of triethylamine/acetic acid in boiling ethanol to give the dispiroindolines **4** with a *trans* configuration of the more bulky substituents at the cyclohexadiene ring. By the same type of transformation the dispiro compounds **7/10** with an additional fused benzene ring are obtained from the pyrylium salt **1a** and **6/9**, the benzo-fused analogues of **3**. Spectroscopic data of the transformation products as well as their mode of formation are discussed.

Ring transformation reactions of heterocycles have been proven to be a powerful tool for the synthesis of a wide range of carbocyclic as well as heterocyclic compounds [2]. Although numerous examples are reported in the literature which proceed with high chemo- and regioselectivity our knowledge on the diastereoselectivity of such reactions is rather small.

Some years ago we have found that 2,4,6-triarylpyrylium salts **1** [3] react with 1-methyl and 1-phenyl substituted 3,3-dimethyl-2-methyleneindolines (Fischer base and derivatives thereof) [4] to yield aroylspiro[cyclohexadiene-indolines] [5] which represent a novel class of photochromic compounds [6]. From the two possible diastereomers only the one with the more bulky substituents in the *trans* position of the cyclohexadiene ring was obtained in high yield. In the same way, the pyrylium salts **1** react with benzo-fused methyleneindolines to give diastereomerically pure aroylspiro[cyclohexadiene-indolines] bearing an additional
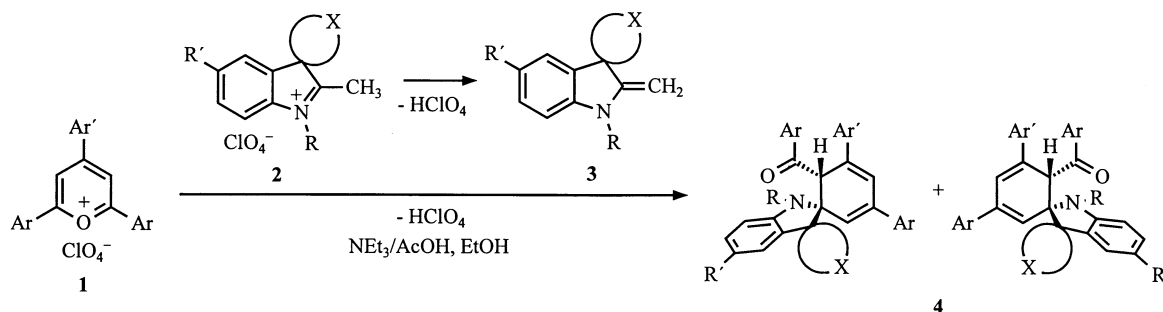
1	2/3	Ar	Ar′	R	R′	X	4
a	a	Ph	Ph	Me	H	(CH$_2$)$_4$	a
b	a	Ph	4-Me-C$_6$H$_4$	Me	H	(CH$_2$)$_4$	b
c	a	Ph	4-MeO-C$_6$H$_4$	Me	H	(CH$_2$)$_4$	c
d	a	Ph	4-Cl-C$_6$H$_4$	Me	H	(CH$_2$)$_4$	d
e	a	Ph	4-Br-C$_6$H$_4$	Me	H	(CH$_2$)$_4$	e
f	a	Ph	4-O$_2$N-C$_6$H$_4$	Me	H	(CH$_2$)$_4$	f
g	a	4-Me-C$_6$H$_4$	Ph	Me	H	(CH$_2$)$_4$	g
h	a	4-Cl-C$_6$H$_4$	Ph	Me	H	(CH$_2$)$_4$	h
i	a	4-Br-C$_6$H$_4$	Ph	Me	H	(CH$_2$)$_4$	i
a	b	Ph	Ph	Me	H	(CH$_2$)$_5$	j
b	b	Ph	4-Me-C$_6$H$_4$	Me	H	(CH$_2$)$_5$	k
d	b	Ph	4-Cl-C$_6$H$_4$	Me	H	(CH$_2$)$_5$	l
g	b	4-Me-C$_6$H$_4$	Ph	Me	H	(CH$_2$)$_5$	m
h	b	4-Cl-C$_6$H$_4$	Ph	Me	H	(CH$_2$)$_5$	n
i	b	4-Br-C$_6$H$_4$	Ph	Me	H	(CH$_2$)$_5$	o
a	c	Ph	Ph	Et	H	(CH$_2$)$_5$	p
a	d	Ph	Ph	i-Pr	H	(CH$_2$)$_5$	q
a	e	Ph	Ph	Ph	H	(CH$_2$)$_5$	r

1	2/3	Ar	Ar'	R	R'	X	4
a	f	Ph	Ph	Me	Me	$(CH_2)_5$	s
a	g	Ph	Ph	Me	i-Pr	$(CH_2)_5$	t
a	h	Ph	Ph	Me	t-Bu	$(CH_2)_5$	u
a	i	Ph	Ph	Me	MeO	$(CH_2)_5$	v
a	j	Ph	Ph	Me	F	$(CH_2)_5$	w
a	k	Ph	Ph	Me	Cl	$(CH_2)_5$	x
a	l	Ph	Ph	Me	Br	$(CH_2)_5$	y
a	m	Ph	Ph	Me	I	$(CH_2)_5$	z
a	n	Ph	Ph	Me	H	$(CH_2)_6$	aa
a	o	Ph	Ph	Me	H	$CH_2C_6H_4(o)CH_2$	bb
a	p	Ph	Ph	Me	H	$(o)C_6H_4C_6H_4(o)$	cc
a	q	Ph	Ph	Me	H	$(CH_2)_2O(CH_2)_2$	dd

benzene ring at the idoline moiety [1]. The transformations could further be extended to chiral methyleneindolines, *i.e.* to compounds with two different substituents at C-3. In this case, from the four possible diastereomers only one was obtained in high yield, the stereochemistry of which can be influenced by the bulkiness of the substituents at C-3 of the methyleneindoline used [7].

Another possibility for structural variations of the indoline part of the aroylspiro[cyclohexadiene-indolines], which is necessary for further elucidation of the influence of structural changes on their photochromic properties, consists in the introduction of an additional spiro-fused carbo- or heterocycle instead of the two substituents at C-3'. These compounds should be available by ring transformation of the pyrylium salts **1** with spiromethyleneindolines of the type **3**, formed *in situ* by deprotonation of the related spiroindolium salts **2**. In this paper we wish to present the results of such investigations.

When the 2,4,6-triarylpyrylium perchlorates **1a-i** and the spiroindolium perchlorate **2a**, possessing a cyclopentane ring at C-3', were refluxed in ethanol in the presence of triethylamine/acetic acid the transformation proceeded as expected to give the dispiro compounds **4a-i** in 76-90% yield. On using the spiroindolium perchlorates **2b-n** with a cyclohexane ring at C-3' and various substituents at the nitrogen and in 5'-position or with a cyloheptane ring at C-3' the dispiroindolines **4j-aa** were obtained (yield 70-95%). The transformations could further be extended to the spiroindolium perchlorates **2o-q**, in which the spiro-fused ring is a benzanellated cycloalkene (**2o,p**) or a heterocycle (**2q**) and to the benzo-fused derivatives **5/8**. They gave rise to the dispiro compounds **4bb-dd**, **7** and **10** in 62-89% yield.

In all examples studied from the two possible diastereomers of **4**, **7** and **10** only that one with the more bulky substituents (ArCO and CX, X = spirocycle) *trans* positioned at the cyclohexadiene ring was formed as a racemate.
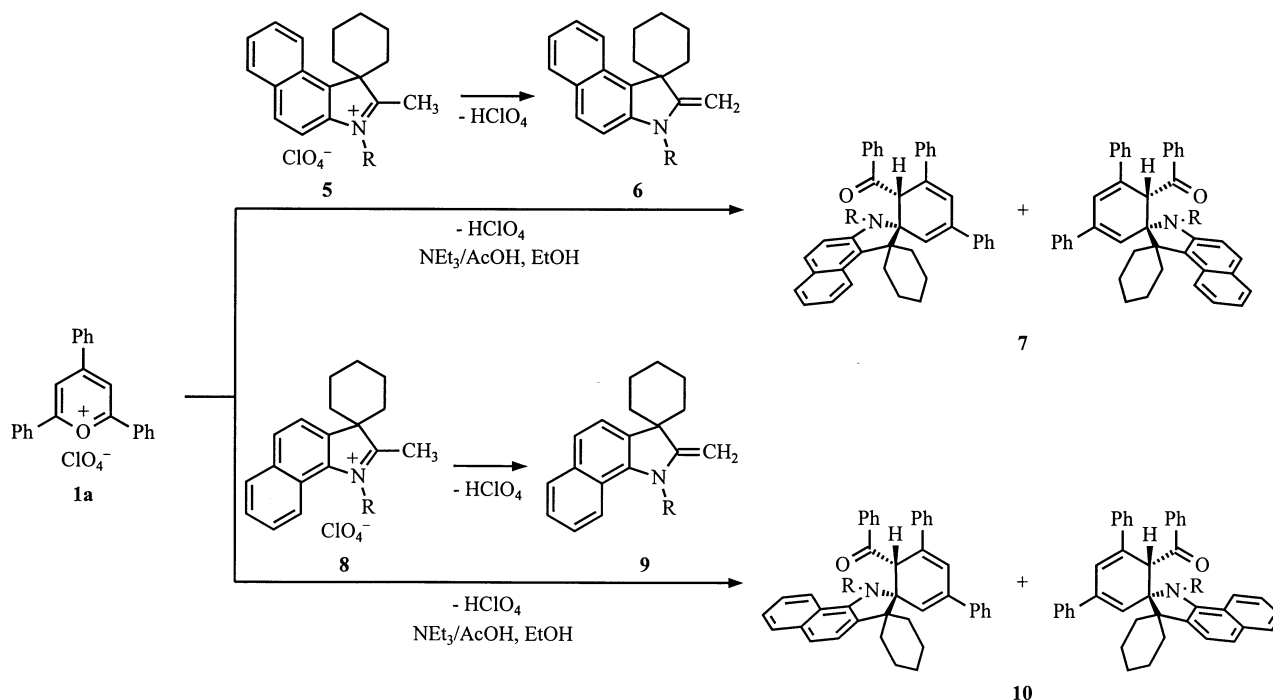
Table 1

Physical and Analytical Data for the Dispiro Compounds **4**, **7** and **10**

No.	Compound	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found		
					C	H	N
4a	6-Benzoyl-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	90	181-182	$C_{37}H_{33}NO$ (507.7)	87.54 87.51	6.55 6.60	2.76 2.77
4b	6-Benzoyl-1'-methyl-5-(4-methylphenyl)-3-phenyldispiro-[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	76	184-185	$C_{38}H_{35}NO$ (521.7)	87.49 87.58	6.76 6.80	3.07 3.10
4c	6-Benzoyl-5-(4-methoxyphenyl)-1'-methyl-3-phenyldispiro-[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	86	177-178	$C_{38}H_{35}NO_2$ (537.7)	84.88 84.60	6.56 6.61	2.60 2.65
4d	6-Benzoyl-5-(4-chlorophenyl)-1'-methyl-3-phenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	82	172-173	$C_{37}H_{32}ClNO$ (542.1)	81.98 82.00	5.95 6.00	2.58 2.68
4e	6-Benzoyl-5-(4-bromophenyl)-1'-methyl-3-phenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	86	158-159	$C_{37}H_{32}BrNO$ (586.6)	75.76 75.80	5.50 5.55	2.39 2.41
4f	6-Benzoyl-1'-methyl-5-(4-nitrophenyl)-3-phenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	88	203-204	$C_{37}H_{32}N_2O_3$ (552.7)	80.41 80.30	5.84 5.90	5.07 5.15
4g	1'-Methyl-6-(4-methylbenzoyl)-3-(4-methylphenyl)-5-phenyl-dispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	78	198-199	$C_{39}H_{37}NO$ (535.7)	87.44 87.50	6.96 7.01	2.61 2.68
4h	6-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-1'-methyl-5-phenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	80	180-181	$C_{37}H_{31}Cl_2NO$ (576.6)	77.08 77.20	5.42 5.51	2.43 2.50
4i	6-(4-Bromobenzoyl)-3-(4-bromophenyl)-1'-methyl-5-phenyld-ispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclopentane]	81	197-198	$C_{37}H_{31}Br_2NO$ (665.5)	66.78 66.85	4.70 4.73	2.10 2.22
4j	6-Benzoyl-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	94	222-223	$C_{38}H_{35}NO$ (521.7)	87.49 87.52	6.76 6.73	2.68 2.70
4k	6-Benzoyl-1'-methyl-5-(4-methylphenyl)-3-phenyldispiro[cyclo-hexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	91	205-206	$C_{39}H_{37}NO$ (535.7)	87.44 87.45	6.96 7.05	2.61 2.55
4l	6-Benzoyl-5-(4-chlorophenyl)-1'-methyl-3-phenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	85	167-168	$C_{38}H_{34}ClNO$ (556.2)	82.07 82.15	6.16 6.23	2.52 2.45
4m	1'-Methyl-6-(4-methylbenzoyl)-3-(4-methylphenyl)-5-phenyl-dispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	90	232-233	$C_{40}H_{39}NO$ (549.8)	87.39 87.48	7.15 7.21	2.55 2.48
4n	6-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-1'-methyl-5-phenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	95	205-206	$C_{38}H_{33}Cl_2NO$ (590.6)	77.28 77.30	5.63 5.70	2.37 2.40
4o	6-(4-Bromobenzoyl)-3-(4-bromophenyl)-1'-methyl-5-phenyld-ispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	92	210-211	$C_{38}H_{33}Br_2NO$ (679.5)	67.17 67.25	4.90 4.92	2.06 2.11
4p	6-Benzoyl-1'-ethyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	92	242-243	$C_{39}H_{37}NO$ (535.7)	87.44 87.30	6.96 7.00	2.61 2.60
4q	6-Benzoyl-1'-isoprpyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	92	188-189	$C_{40}H_{39}NO$ (549.8)	87.39 87.41	7.15 7.20	2.55 2.50
4r	6-Benzoyl-1',3,5-triphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	70	237-238	$C_{43}H_{37}NO$ (583.8)	88.47 88.50	6.39 6.41	2.40 2.45
4s	6-Benzoyl-1',5'-dimethyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	88	211-212	$C_{39}H_{37}NO$ (535.7)	87.44 87.50	6.96 7.00	2.61 2.70
4t	6-Benzoyl-5'-isopropyl-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	95	230-231	$C_{41}H_{41}NO$ (563.8)	87.35 87.30	7.33 7.40	2.48 2.55
4u	6-Benzoyl-5'-*tert*-butyl-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	84	234-235	$C_{42}H_{43}NO$ (577.8)	87.31 87.45	7.50 7.53	2.42 2.48
4v	6-Benzoyl-5'-methoxy-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	92	218-219	$C_{39}H_{37}NO_2$ (551.7)	84.90 84.90	6.76 6.82	2.54 2.60
4w	6-Benzoyl-5'-fluoro-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	93	218-219	$C_{38}H_{34}FNO$ (539.7)	84.57 84.62	6.35 6.41	2.60 2.55
4x	6-Benzoyl-5'-chloro-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	82	226-227	$C_{38}H_{34}ClNO$ (556.2)	82.07 82.22	6.16 6.20	2.52 2.43
4y	6-Benzoyl-5'-bromo-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	92	227-228	$C_{38}H_{34}BrNO$ (600.6)	75.99 76.00	5.71 5.82	2.33 2.30
4z	6-Benzoyl-5'-iodo-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',1"-cyclohexane]	90	239-240	$C_{38}H_{34}INO$ (647.6)	70.48 70.53	5.29 5.36	2.16 2.20
4aa	6"-Benzoyl-1'-methyl-3",5"-diphenyldispiro[cycloheptane-1,3'-indo-line-2',1"-cyclohexa-[2.4]diene]	95	229-230	$C_{39}H_{37}NO$ (535.7)	87.44 87.39	6.96 7.01	2.99 2.90
4bb	6-Benzoyl-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',2"-indane]	89	206-207	$C_{41}H_{33}NO$ (555.7)	88.62 88.61	5.99 6.03	2.52 2.55
4cc	6-Benzoyl-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',9"-fluorene]	81	189-190	$C_{45}H_{33}NO$ (603.8)	89.52 89.61	5.01 5.11	2.32 2.40
4dd	6-Benzoyl-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-indoline-3',4"-tetrahydropyrane]	78	228-229	$C_{37}H_{33}NO_2$ (523.7)	84.86 84.70	6.35 6.41	2.67 2.70
7	6-Benzoyl-3'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-benzo[e]indole-1',1"-cyclohexane]	76	187-188	$C_{42}H_{37}NO$ (571.8)	88.23 88.30	6.52 6.58	2.45 2.41
10	6-Benzoyl-1'-methyl-3,5-diphenyldispiro[cyclohexa-2,4-diene-1,2'-benzo[g]indoel-3',1"-cyclohexane]	62	228-229	$C_{42}H_{37}NO$ (571.8)	88.23 88.11	6.52 6.48	2.45 2.51

Table 2
Spectral Data for the Dispiro Compounds **4**, **7** and **10**

Compound	IR (KBr) (cm^{-1}) CO	UV (CH$_3$CN) λ_{max} (nm) (log ε)	^{1}H-NMR (deuteriochloroform) [a] δ (ppm)
4a [b],[c]	1677	254 (4.61), 311 (4.02), 410 sh (2.98)	1.29-2.28 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.45 (s, 3H, 1'-CH$_3$), 5.37 (s, 1H, 6-H), 5.53 (d, 1H, 7'-H), 5.94 (s, 1H, 2-H), 6.81 (s, 1H, 4-H), 6.55-7.60 (m, 18H, arom-H)
4b	1676	254 (4.62), 311 sh (4.08), 417 sh (3.00)	1.27-2.28 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.14 (s, 3H, 5-CH$_3$C$_6$H$_4$), 2.45 (s, 3H, 1'-CH$_3$), 5.37 (s, 1H, 6-H), 5.53 (d, 1H, 7'-H), 5.92 (s, 1H, 2-H), 6.79 (s, 1H, 4-H), 6.54-7.61 (m, 17H, arom-H)
4c	1676	251 (4.57), 270 sh (4.47), 315 (4.11), 417 sh (3.13)	1.25-2.34 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.45 (s, 3H, 1'-CH$_3$), 3.60 (s, 3H, 5-CH$_3$OC$_6$H$_4$), 5.35 (s, 1H, 6-H), 5.53 (d, 1H, 7'-H), 5.89 (s, 1H, 2-H), 6.73 (s, 1H, 4-H), 6.54-7.61 (m, 17H, arom-H)
4d	1677	256 (4.64), 314 (4.09), 417 sh (3.06)	1.26-2.29 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.45 (s, 3H, 1'-CH$_3$), 5.32 (s, 1H, 6-H), 5.53 (d, 1H, 7'-H), 5.96 (s, 1H, 4-H), 6.54-7.59 (m, 17H, arom-H)
4e	1677	256 (4.63), 314 (4.08), 417 sh (3.06)	1.26-2.30 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.45 (s, 3H, 1'-CH$_3$), 5.31 (s, 1H, 6-H), 5.54 (d, 1H, 7'-H), 5.96 (s, 1H, 2-H), 6.80 (s, 1H, 4-H), 6.55-7.60 (m, 18H, arom-H)
4f	1676	251 (4.55), 370 (4.03), 455 sh (3.24)	1.29-2.27 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.47 (s, 3H, 1'-CH$_3$), 5.36 (s, 1H, 6-H), 5.56 (d, 1H, 7'-H), 6.06 (s, 1H, 2-H), 6.98 (s, 1H, 4-H), 6.56-7.97 (m, 17H, arom-H)
4g	1675	261 (4.70), 314 (4.02), 417 sh (3.04)	1.24-2.22 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.25 (s, 3H, 3-CH$_3$C$_6$H$_4$), 2.32 (s, 3H, 6-CH$_3$C$_6$H$_4$CO), 2.45 (s, 3H, 1'-CH$_3$), 5.31 (s, 1H, 6-H), 5.58 (d, 1H, 7'-H), 5.90 (s, 1H, 2-H), 6.79 (s, 1H, 4-H), 6.53-7.50 (m, 16H, arom-H)
4h	1678	260 (4.72), 314 sh (4.02), 424 sh (2.95)	1.29-2.25 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.45 (s, 3H, 1'-CH$_3$), 5.30 (s, 1H, 6-H), 5.59 (d, 1H, 7'-H), 5.91 (s, 1H, 2-H), 6.73 (s, 1H, 4-H), 6.57-7.51 (m, 16H, arom-H)
4i	1678	263 (4.76), 313 sh (4.04), 417 sh (3.04)	1.23-2.28 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.45 (s, 3H, 1'-CH$_3$), 5.29 (s, 1H, 6-H), 5.59 (d, 1H, 7'-H), 5.92 (s, 1H, 2-H), 6.72 (s, 1H, 4-H), 6.56-7.50 (m, 16H, arom-H)
4j [b],[c]	1678	255 (4.61), 309 sh (4.04), 417 sh (3.08)	1.09-1.91 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.46 (s, 3H, 1'-CH$_3$), 5.30 (s, 1H, 6-H), 5.48 (d, 1H, 7'-H), 5.96 (s, 1H, 2-H), 6.81 (s, 1H, 4-H), 6.53-7.63 (m, 18H, arom-H)
4k	1679	255 (4.63), 313 sh (4.10), 417 sh (3.06)	0.99-2.04 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.14 (s, 3H, 5-CH$_3$C$_6$H$_4$), 2.46 (s, 3H, 1'-CH$_3$), 5.30 (s, 1H, 6-H), 5.49 (d, 1H, 7'-H), 5.93 (s, 1H, 2-H), 6.78 (s, 1H, 4-H), 6.53-7.63 (m, 17H, arom-H)
4l	1678	256 (4.63), 312 (4.10), 417 sh (3.15)	1.02-1.97 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.46 (s, 3H, 1'-CH$_3$), 5.25 (s, 1H, 6-H), 5.49 (d, 1H, 7'-H), 5.97 (s, 1H, 2-H), 6.79 (s, 1H, 4-H), 6.54-7.62 (m, 17H, arom-H)
4m	1675	261 (4.67), 311 (4.02), 413 sh (3.13)	1.06-1.90 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.27 (s, 3H, 3-CH$_3$C$_6$H$_4$), 2.34 (s, 3H, 6-CH$_3$C$_6$H$_4$CO), 2.46 (s, 3H, 1'-CH$_3$), 5.23 (s, 1H, 6-H), 5.54 (d, 1H, 7'-H), 5.91 (s, 1H, 2-H), 6.79 (s, 1H, 4-H), 6.52-7.53 (m, 16H, arom-H)
4n	1677	261 (4.74), 311 sh (4.07), 424 sh (3.16)	1.05-2.00 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.45 (s, 3H, 1'-CH$_3$), 5.23 (s, 1H, 6-H), 5.55 (d, 1H, 7'-H), 5.93 (s, 1H, 2-H), 6.73 (s, 1H, 4-H), 6.55-7.54 (m, 16H, arom-H)
4o	1677	263 (4.77), 313 sh (4.06), 417 sh (3.11)	1.11-1.97 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.45 (s, 3H, 1'-CH$_3$), 5.22 (s, 1H, 6-H), 5.56 (d, 1H, 7'-H), 5.93 (s, 1H, 2-H), 6.72 (s, 1H, 4-H), 6.56-7.50 (m, 16H, arom-H)
4p	1676	254 (4.54), 313 (3.94), 417 sh (3.06)	0.89 (t, 3H, 1'-CH$_2$CH$_3$), 1.09-2.00 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.46 (m, 1H, 1'-CH$_2$CH$_3$), 3.05 (m, 1H, 1'-CH$_2$CH$_3$), 5.30 (s, 1H, 6-H), 5.42 (d, 1H, 7'-H), 5.92 (s, 1H, 2-H), 6.80 (s, 1H, 4-H), 6.51-7.63 (m, 18H, arom-H)
4q	1679	252 (4.56), 311 (4.00), 410 sh (3.22)	0.82 (d, 3H, 1-CH(CH$_3$)$_2$), 1.14 (d, 3H, 1-CH(CH$_3$)$_2$), 1.26-2.01 (m, 10H, 3',3'-(CH$_2$)$_5$), 3.67 (m, 1H, 1-CH(CH$_3$)$_2$), 5.36 (s, 1H, 6-H), 6.00 (s, 1H, 2-H), 6.19 (d, 1H, 7'-H), 6.76 (s, 1H, 4-H), 6.59-7.63 (m, 18H, arom-H)
4r	1679	254 (4.57), 291 (4.24), 314 sh (4.22), 400 sh (3.06)	1.02-2.01 (m, 10H, 3',3'-(CH$_2$)$_5$), 5.29 (s, 1H, 6-H), 5.72 (d, 1H, 2-H), 5.84 (d, 1H, 7'-H), 6.88 (s, 1H, 4-H), 6.70-7.52 (m, 18H, arom-H)
4s	1677	254 (4.57), 316 (3.98), 420 sh (3.04)	1.11-1.91 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.25 (s, 3H, 5'-CH$_3$), 2.45 (s, 3H, 1'-CH$_3$), 5.28 (s, 1H, 6-H), 5.40 (d, 1H, 7'-H), 5.96 (s, 1H, 2-H), 6.80 (s, 1H, 4-H), 6.64-7.64 (m, 17H, arom-H)
4t	1678	254 (4.65), 313 sh (4.06), 420 sh (3.10)	1.21 (d, 3H, 5'-CH(CH$_3$)$_2$), 1.23 (d, 3H, 5'-CH(CH$_3$)$_2$), 1.08-2.02 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.46 (s, 3H, 1'-CH$_3$), 2.81 (m, 1H, 5'-CH(CH$_3$)$_2$), 5.29 (s, 1H, 6-H), 5.40 (d, 1H, 7'-H), 5.96 (s, 1H, 2-H), 6.80 (s, 1H, 4-H), 6.68-7.63 (m, 17H, arom-H)
4u	1678	254 (4.60), 313 (4.00), 417 sh (3.00)	1.14-2.00 (m, 10H, 3',3'-(CH$_2$)$_5$), 1.29 (s, 9H, 5'-C(CH$_3$)$_3$), 2.46 (s, 3H, 1'-CH$_3$), 5.29 (s, 1H, 6-H), 5.40 (d, 1H, 7'-H), 5.96 (s, 1H, 2-H), 6.80 (s, 1H, 4-H), 6.84-7.64 (m, 17H, arom-H)
4v	1677	258 (4.70), 329 sh (4.00), 424 sh (3.00)	1.08-1.93 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.45 (s, 3H, 1'-CH$_3$), 3.73 (s, 3H, 5'-CH$_3$), 5.27 (s, 1H, 6-H), 5.37 (d, 1H, 7'-H), 5.95 (s, 1H, 2-H), 6.80 (s, 1H, 6-H), 6.41-7.63 (m, 17H, arom-H)
4w	1678	253 (4.60), 317 (3.99), 407 sh (3.18)	1.09-1.94 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.44 (s, 3H, 1'-CH$_3$), 5.28 (s, 1H, 6-H), 5.31 (m, 1H, 7'-H), 5.92 (s, 1H, 2-H), 6.80 (s, 1H, 4-H), 6.50-7.63 (m, 17H, arom-H)
4x	1678	254 (4.57), 314 (3.99), 407 sh (3.15)	1.08-1.98 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.43 (s, 3H, 1'-CH$_3$), 5.29 (s, 1H, 6-H), 5.35 (d, 1H, 7'-H), 5.89 (s, 1H, 2-H), 6.81 (s, 1H, 4-H), 6.77-7.63 (m, 17H, arom-H)
4y	1678	254 (4.57), 316 sh (4.00), 417 sh (3.15)	1.09-1.99 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.42 (s, 3H, 1'-CH$_3$), 5.29 (s, 1H, 6-H), 5.31 (d, 1H, 7'-H), 5.88 (s, 1H, 2-H), 6.79 (s, 1H, 4-H), 6.91-7.61 (m, 17H, arom-H)
4z	1678	256 (4.59), 269 sh (4.52), 313 sh (4.01), 410 sh (3.01)	1.09-1.99 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.43 (s, 3H, 1'-CH$_3$), 5.25 (d, 1H, 7'-H), 5.29 (s, 1H, 6-H), 5.88 (s, 1H, 2-H), 6.79 (s, 1H, 4-H), 7.09-7.61 (m, 17H, arom-H)
4aa [b],[c]	1678	254 (4.58), 313 (3.99), 417 sh (2.95)	1.32-2.17 (m, 12H, 3',3'-(CH$_2$)$_6$), 2.42 (s, 3H, 1'-CH$_3$), 5.24 (s, 1H, 6''-H), 5.50 (d, 1H, 7'-H), 6.00 (s, 1H, 2''-H), 6.83 (s, 1H, 4''-H), 6.54-7.62 (m, 18H, arom-H)
4bb [b],[c]	1678	253 (4.62), 313 sh (4.04), 410 sh (3.00)	2.47 (s, 3H, 1'-CH$_3$), 2.59 (d, J = 10.0 Hz, 1H, 3',3'-(CH$_2$)$_2$C$_6$H$_4$), 3.21 (d, J = 10.2 Hz, 1H, 3',3'-(CH$_2$)$_2$C$_6$H$_4$), 3.61 (d, J = 10.0 Hz, 1H, 3',3'-(CH$_2$)$_2$C$_6$H$_4$), 3.64 (d, J = 10.2 Hz, 1H, 3',3'-(CH$_2$)$_2$C$_6$H$_4$), 2.47 (s, 3H, 1'-CH$_3$), 5.39 (s, 1H, 6-H), 5.60 (d, 1H, 7'-H), 5.98 (s, 1H, 2-H), 6.79 (s, 1H, 4-H), 6.35-7.57 (m, 22H, arom-H)

Table 2 (Continued)

Compound	IR (KBr) (cm^{-1}) CO	UV (CH$_3$CN) λ_{max} (nm) (log ε)	^{1}H-NMR (deuteriochloroform) [a] δ (ppm)
4cc [b],[c]	1678	254 (4.70), 314 sh (4.02), 400 sh (2.95)	2.51 (s, 3H, 1'-CH$_3$), 5.39 (s, 1H, 6-H), 5.55 (s, 1H, 2-H), 6.13 (s, 1H, 4-H), 6.22 (d, 1H, 7'-H), 6.51-7.98 (m, 26H, arom-H)
4dd	1678	254 (4.58), 313 (3.99), 417 sh (2.95)	1.59 (d, 1H, 3',3'-(CH_2CH$_2$)$_2$O), 1.86 (d, 1H, 3',3'-(CH_2CH$_2$)$_2$O), 2.10-2.39 (m, 2H, 3',3'-(CH$_2$CH_2)$_2$O), 2.47 (s, 3H, 1'-CH$_3$), 3.43-4.11 (m, 4H, 3',3'-(CH$_2$CH_2)$_2$O), 5.27 (s, 1H, 6-H), 5.54 (d, 1H, 7'-H), 5.92 (s, 1H, 2-H), 6.83 (s, 1H, 4-H), 6.57-7.63 (m, 18H, arom-H)
7	1677	218 sh (4.63), 257 (4.82), 304 sh (4.20), 315 (4.26), 397 sh (3.64)	1.38-2.98 (m, 10H, 1',1'-(CH$_2$)$_5$), 2.60 (s, 3H, 3'-CH$_3$), 5.58 (s, 1H, 6-H), 5.82 (d, 1H, 4'-H), 6.19 (s, 1H, 2-H), 6.92 (s, 1H, 4-H), 7.03-8.12 (m, 20H, arom-H)
10	1677	254 (4.68), 325 (4.01), 350 sh (3.98)	1.13-1.96 (m, 10H, 3',3'-(CH$_2$)$_5$), 3.10 (s, 3H, 1'-CH$_3$), 5.23 (s, 1H, 6-H), 6.22 (s, 1H, 2-H), 6.81 (s, 1H, 4-H), 6.63-7.67 (m, 21H, arom-H)

[a] 2-H, 2''-H, 4-H, 4'-H, 4''-H, 6-H, 6''-H and 7'-H denote the protons in 2-, 2''-, 4-, 4'-, 4''-, 6-, 6''- and 7'-position, respectively, and arom-H the protons bonded to the benzene rings. [b] ^{13}C nmr (deuteriochloroform) **4a** 21.4, 22.4, 28.6, 33.8 (3',3'-(CH$_2$)$_4$), 29.2 (1'-CH$_3$), 45.2 (C-6), 64.2 (C-3'), 75.2 (C-1), 103.5, 114.4, 121.0, 121.5, 122.2, 123.5, 124.1, 125.9, 126.3, 126.5, 126.6, 126.7, 130.7, 134.3, 134.5, 136.9, 137.0, 137.6, 138.3, 146.9 (olefinic and aromatic carbons), 195.3 (6-COPh), **4j** 19.8, 21.8, 24.0, 27.8, 31.0 (3',3'-(CH$_2$)$_5$), 29.5 (1'-CH$_3$), 43.6 (C-6), 56.8 (C-3'), 77.0 (C-1), 104.0, 114.0, 121.2, 122.5, 123.5, 124.3, 124.6, 125.8, 125.9, 126.0, 126.5, 126.7, 126.8, 130.8, 132.7, 134.2, 137.1, 137.2, 137.9, 138.6, 147.6 (olefinic and aromatic carbons), 195.8 (6-COPh), **4aa** 21.0, 22.2, 29.5, 30.0, 30.2, 33.0 (3',3'-(CH$_2$)$_6$), 29.2 (1'-CH$_3$), 44.9 (C-6''), 58.3 (C-3'), 77.2 (C-1''), 103.4, 103.9, 114.3, 117.7, 121.1, 121.9, 122.9, 123.1, 124.0, 125.8, 126.0, 126.3, 126.6, 126.7, 130.7, 134.2, 134.8, 136.5, 137.1, 137.5, 138.4, 146.6 (olefinic and aromatic carbons), 195.0 (6''-COPh), **4bb** 29.1 (1'-CH$_3$), 36.7, 40.5 (3',3'-(CH$_2$)$_2$C$_6$H$_4$), 45.0 (C-6), 63.3 (C-3'), 74.7 (C-1), 103.7, 114.6, 120.3, 121.0, 121.6, 122.7, 123.0, 123.4, 124.1, 124.4, 124.6, 125.9, 126.0, 126.2, 126.4, 126.5, 126.7, 130.9, 133.6, 134.3, 136.7, 136.9, 138.0, 138.2, 139.5, 140.2, 146.7 (olefinic and aromatic carbons), 194.9 (6-COPh), **4cc** 32.1 (1'-CH$_3$), 47.1 (C-6), 69.3 (C-3'), 81.3 (C-1), 106.3, 116.4, 117.5, 118.1, 120.6, 121.4, 122.3, 123.0, 123.5, 123.6, 124.1, 124.3, 124.9, 125.3, 125.5, 125.8, 125.9, 126.3, 126.6, 126.8, 126.9, 130.0, 131.0, 135.4, 135.5, 136.7, 138.0, 138.7, 138.8, 139.1, 144.8, 145.3, 150.4 (olefinic and aromatic carbons), 194.9 (6-COPh), [c] Mass spectra: (70 eV), m/z (%) **4a** 507 (58) [M$^+$], 402 (80) [M$^+$-PhCO], 105 (46) [PhCO$^+$], 91 (100), 77 (32) [Ph$^+$], **4j** 521 (100) [M$^+$], 416 (39) [M$^+$-PhCO], 105 (63) [PhCO$^+$], 77 (55) [Ph$^+$], **4aa** 535 (34) [M$^+$], 430 (31) [M$^+$-PhCO], 91 (100), **4bb** 555 (43) [M$^+$], 450 (58) [M$^+$-PhCO], 306 (100), 105 (42) [PhCO$^+$], 77 (29) [Ph$^+$], **4cc** 604 (80) [M$^+$], 499 (69) [M$^+$-PhCO], 105 (100) [PhCO$^+$], 77 (40) [Ph$^+$].

One may assume that in the course of the pyrylium ring transformations the cation of the spiroindolium salts **2, 5** and **8** is deprotonated to the corresponding methyleneindoline **3, 6** and **9**, respectively, acting as carbon nucleophile of the enamine type as already discussed for related reactions of the salts **1** with other methyleneindolines [1,5,7]. The 2*H*-pyran derivative formed [8] as the result of the attack at the preferred position 2 of **1** [3] is then ring opened by an electrocyclic reaction to a merocyanine which recyclizes finally by another electrocyclic process to the dispiro compounds **4, 7** and **10** [9]. Since the cyclohexadiene moiety is built up from four carbon atoms of the pyrylium cation and two C-atoms of the spiromethyleneindoline by connection of the former positions 2 and 4 of **1** by a C$_2$-chain the reaction can be classified as a 2,5-[C$_4$+C$_2$] transformation [10].

The results of elemental analyses and spectroscopic data are in agreement with the structure proposed for the dispiro compounds **4/7/10**. In the ^{1}H nmr spectra the broad multiplet at 0.99-2.34 ppm can be attributed to the protons of the spiro-fused cyclopentane, cyclohexane and cycloheptane, respectively, present in **4a-aa**, **7** and **10**. Cooling a solution of **4a**, **4j** and **4aa** in deuterated methylenechloride to -90° does not lead to sharp signals of these protons indicating a high conformational flexibility of the cycloalkane moiety even at low temperatures. The protons of the *N*-methyl group of **4a-o** and **4s-dd** show the expected singlet at 2.42-3.10 ppm. The aromatic proton adjacent to the nitrogen causes a doublet at 5.29-6.22 ppm. This signal is significantly shifted upfield in comparison to the multiplet of the other protons bonded at the benzene rings (6.35-8.12 ppm) by the known shielding effect of the NR-group (R = alkyl) [11]. The signals of the protons of the cyclohexadiene part of the molecule can be located as a singlet at 5.22-5.58 ppm (methine proton) and two singlets at 5.55-6.98 ppm (olefinic protons). The presence of the carbonyl group is documented in the ir spectra by a strong C=O-vibration band at 1675-1679 cm^{-1} [12] and, as shown for **4a**, **4j** and **4aa-cc**, by the typical signal of the carbonyl carbon in the ^{13}C nmr spectra around 195 ppm. Finally, the uv-vis spectra show an absorption at 251-263 nm of high intensity accompanied by up to three smaller bands at longer wavelengths.

All spectroscopic parameters determined for the dispiro compounds **4, 7** and **10** are comparable to those obtained for the structurally related diastereomerically pure aroylspiro[cyclohexadiene-indolines] with two identical or different substituents at C-3' [5,7] as well as for their benzofused analogues [1]. The structure of these compounds were additionally confirmed by X-ray structure determinations that clearly show a *trans* configuration of the more bulky substituents at the cyclohexadiene ring. Hence, it can be concluded that, as a result of the ring transformations **1** + **3** → **4** and **1a** + **6/9** → **7/10**, the diastereomer is formed, where ArCO and CX (X = spirocycle) also have a *trans* configuration.

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, ir spectra were obtained on a ATI Mattson Genesis FTIR spectrophotometer (in potassium bromide) and uv-vis spectra on a Zeiss M 40 instrument (acetonitrile, 25°). Mass spectra were determined on a Varian MAT 212 spectrometer (70 eV, electron impact). The pyrylium perchlorates **1a** [13], **1b** [14], **1c** [15], **1d,f** [16], **1e** [17], **1g-i** [18], *N*-ethyl-*N*-phenylhydrazine [19], *N*-isopropyl-*N*-phenylhydrazine [19], 1-naphthylhydrazine [20], 2-naphthylhydrazine [20], 1-cylopentylethanone [21], 1-cycloheptylethanone [22], 1-(9*H*-fluoren-9-yl)ethanone [23] and 1-(tetrahydropyran-4-yl)ethanone [24] were synthesized according to literature procedures. The preparation of the spiroindolium perchlorates **2b** and **2o** was reported in a previous paper [25]. *N*-Methyl-*N*-phenylhydrazine, *N,N*-diphenyl-hydrazine hydrochloride, 4-methylphenylhydrazine hydrochloride, 4-fluorophenylhydrazine hydrochloride, 4-chlorophenylhydrazine hydrochloride and 4-bromophenylhydrazine hydrochloride were purchased from Aldrich, 4-isopropylphenylhydrazine hydrochloride and 4-methoxyphenylhydrazine hydrochloride from Acros, 4-*tert*-butylphenylhydrazine hydrochloride as well as 4-iodophenyl-hydrazine from Lancaster and 1-cyclohexylethanone from Fluka.

Preparation of the Starting Spiroindolium Perchlorates 2 from Hydrazines and Ketones

a) By an One-pot Procedure.

The spiroindolium perchlorates **2a**, **2c-e**, **2n**, **2p** and **2q** were obtained from *N*-substituted *N*-phenylhydrazines or their hydrochlorides, α-branched ketones and perchloric acid in boiling ethanol applying a previously reported procedure [25] which combines the hydrazone formation and the Fischer indolization [26] to an one-pot synthesis.

1',2'-Dimethylspiro[cyclopentane-1,3'-indolium] Perchlorate (**2a**).

This compound was obtained from *N*-methyl-*N*-phenylhy-drazine, 1-cyclopentylethanone and perchloric acid in 61% yield, mp 210-211° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfox-ide): δ 1.89-2.36 (m, 8H, 3',3'-(CH$_2$)$_4$), 2.78 (s, 3H, 2'-CH$_3$), 3.99 (s, 3H, 1'-CH$_3$), 7.60-7.92 (m, 4H, arom-H).

Anal. Calcd. for C$_{14}$H$_{18}$ClNO$_4$: C, 56.10; H, 6.05; N, 4.67. Found: C, 56.20; H, 6.10; N, 4.51.

1'-Ethyl-2'-methylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2c**).

This compound was obtained from *N*-ethyl-*N*-phenylhydrazine, 1-cyclohexylethanone and perchloric acid in 74% yield, mp 188-189° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.40 (t, 3H, 1'-CH$_2$C*H*$_3$), 1.44-2.04 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.81 (s, 3H, 2'-CH$_3$), 4.46 (q, 2H, 1'-C*H*$_2$CH$_3$), 7.52-8.08 (m, 4H, arom-H).

Anal. Calcd. for C$_{16}$H$_{22}$ClNO$_4$: C, 58.62; H, 6.76; N, 4.27. Found: C, 58.70; H, 6.71; N, 4.31.

1'-Isopropyl-2'-methylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2d**).

This compound was obtained from *N*-isopropyl-*N*-phenylhy-drazine, 1-cyclohexylethanone and perchloric acid in 68% yield,

mp 215-216° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfox-ide): δ 1.67 (d, 6H, 1'-CH(C*H*$_3$)$_2$), 1.33-2.05 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.84 (s, 3H, 2'-CH$_3$), 5.11 (m, 1H, 1'-C*H*(CH$_3$)$_2$), 7.53-8.11 (m, 4H, arom-H).

Anal. Calcd. for C$_{17}$H$_{24}$ClNO$_4$: C, 59.73; H, 7.08; N, 4.10. Found: C, 59.80; H, 7.20; N, 4.10.

2'-Methyl-1'-phenylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2e**) [27].

This compound was obtained from *N,N*-diphenylhydrazine hydrochloride, 1-cyclohexylethanone and perchloric acid in 61% yield, mp 221-222° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sul-foxide): δ 1.52-2.09 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.64 (s, 3H, 2'-CH$_3$), 7.05-8.17 (m, 9H, arom-H).

Anal. Calcd. for C$_{20}$H$_{22}$ClNO$_4$: C, 63.91; H, 5.90; N, 3.73. Found: C, 64.00; H, 5.92; N, 3.80.

1',2'-Dimethylspiro[cycloheptane-1,3'-indolium] Perchlorate (**2n**).

This compound was obtained from *N*-methyl-*N*-phenylhy-drazine, 1-cycloheptylethanone and perchloric acid in 35% yield, mp 202-203° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfox-ide): δ 1.54-2.09 (m, 12H, 3',3'-(CH$_2$)$_6$), 2.75 (s, 3H, 2'-CH$_3$), 3.89 (s, 3H, 1'-CH$_3$), 7.52-7.91 (m, 4H, arom-H).

Anal. Calcd. for C$_{16}$H$_{22}$ClNO$_4$: C, 58.62; H, 6.76; N, 4.27. Found: C, 58.60; H, 6.95; N, 4.30.

1',2'-Dimethylspiro[fluorene-9,3'-indolium] Perchlorate (**2p**).

This compound was obtained from *N*-methyl-*N*-phenylhy-drazine, 1-(9*H*-fluoren-9-yl)ethanone and perchloric acid in 54% yield, mp 201-202° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sul-foxide): δ 2.14 (s, 3H, 2'-CH$_3$), 4.20 (s, 3H, 1'-CH$_3$), 6.88-8.13 (m, 12H, arom-H).

Anal. Calcd. for C$_{22}$H$_{18}$ClNO$_4$: C, 66.75; H, 4.58; N, 3.54. Found: C, 66.80; H, 4.51; N, 3.60.

1,2-Dimethylspiro[indolium-3,4'-tetrahydrofuran] Perchlorate (**2q**).

This compound was obtained from *N*-methyl-*N*-phenyl-hydrazine, 1-(tetrahydropyran-4-yl)ethanone and perchloric acid in 40% yield, mp 238-239° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.41 (d, 2H, 3,3-(C*H*$_2$CH$_2$)$_2$O), 2.20 (m, 2H, 3,3-(CH$_2$CH$_2$)$_2$O), 2.75 (s, 3H, 2-CH$_3$), 3.91 (s, 3H, 1-CH$_3$), 3.95 (m, 4H, 3,3-(CH$_2$C*H*$_2$)$_2$O), 7.51-8.28 (m, 4H, arom-H).

Anal. Calcd. for C$_{14}$H$_{18}$ClNO$_5$: C, 53.26; H, 5.75; N, 4.44. Found: C, 58.30; H, 5.80; N, 4.50.

b) Via Spiroindoles.

The spiroindolium perchlorates **2f-m**, **5** and **8** were prepared from *N*-arylhydrazines or their hydrochlorides and α-branched ketones by the following two step procedure consisting of a Fischer type reaction [26] to spiroindoles and a subsequent methylation with dimethyl sulfate.

Synthesis of the Spiroindoles.

To 20 ml of absolute ethanol, 20 mmoles *N*-arylhydrazine or its hydrochloride, 2.52 g (20 mmoles) 1-cyclo-hexylethanone and perchloric acid (5.74 g, 40 mmoles, if the free hydrazine is used, 2.87 g, 20 mmoles, in the case of its hydrochloride) were added. The reaction mixture was then magnetically stirred under reflux for two hours, cooled to room temperature and poured into 100 ml of a stirred solution

of sodium hydroxide in water (10%). After transfer into a separatory funnel, the product was extracted three times with chloroform (30 ml), the combined organic layers were washed two times with water (50 ml), dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The resulting crude spiroindoles were used without further purification for the next reaction step.

Synthesis of Spiroindolium Perchlorates.

The methylation of the spiroindoles was performed in toluene with dimethyl sulfate followed by precipitation of the spiroindolium perchlorates with perchloric acid from an ethanol solution as recently reported [1].

1',2',5'-Trimethylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2f**).

4-Methylphenylhydrazine hydrochloride was reacted with 1-cyclohexylethanone to give 2',5'-dimethylspiro[cyclohexane-1,3'-indole] (yield 95%), which was methylated to **2f**, yield 26%, mp 249-250° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.32-1.98 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.42 (s, 3H, 5'-CH$_3$), 2.69 (s, 3H, 2'-CH$_3$), 3.88 (s, 3H, 1'-CH$_3$), 7.40-7.85 (m, 3H, arom-H).

Anal. Calcd. for C$_{16}$H$_{22}$ClNO$_4$: C, 58.62; H, 7.25; N, 4.27. Found: C, 58.67; H, 7.10; N, 4.30.

5'-Isopropyl-1',2'-dimethylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2g**).

4-Isopropylphenylhydrazine was reacted with 1-cyclohexylethanone to give 5'-isopropyl-2'-methylspiro[cyclohexane-1,3'-indole] (yield 96%), which was methylated to **2g**, yield 39%, mp 186-187° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.21 (d, 6H, 5'-CH(CH_3)$_2$), 1.34-2.00 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.71 (s, 3H, 2'-CH$_3$), 3.06 (m, 1H, 5'-CH(CH$_3$)$_2$), 3.90 (s, 3H, 1'-CH$_3$), 7.48-7.82 (m, 3H, arom-H).

Anal. Calcd. for C$_{18}$H$_{26}$ClNO$_4$: C, 60.75; H, 7.36; N, 3.94. Found: C, 60.80; H, 7.31; N, 3.80.

5'-*tert*-Butyl-1',2'-dimethylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2h**).

4-*tert*-Butylphenylhydrazine hydrochloride was reacted with 1-cyclohexylehanone to give 5'-*tert*-butyl-2'-methylspiro[cyclohexane-1,3'-indole] (yield 94 %), which was methylated to **2h**, yield 43%, mp 267-268° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.31 (s, 9H, 5'-C(CH$_3$)$_3$), 1.33-2.01 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.72 (s, 3H, 2'-CH$_3$), 3.90 (s, 3H, 1'-CH$_3$), 7.62-7.88 (m, 3H, arom-H).

Anal. Calcd. for C$_{19}$H$_{28}$ClNO$_4$: C, 61.70; H, 7.63; N, 3.79. Found: C, 61.80; H, 7.50; N, 3.80.

5'-Methoxy-1',2'-dimethylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2i**).

4-Methoxyphenylhydrazine hydrochloride was reacted with 1-cyclohexylethanone to give 5'-methoxy-2'-methylspiro[cyclohexane-1,3'-indole] (yield 84%), which was methylated to **2i**, yield 26%, mp 223-224° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.32-1.99 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.65 (s, 3H, 2'-CH$_3$), 3.82 (s, 3H, 5'-OCH$_3$), 3.86 (s, 3H, 1'-CH$_3$), 7.12-7.81 (m, 3H, arom-H).

Anal. Calcd. for C$_{16}$H$_{22}$ClNO$_5$: C, 55.90; H, 6.45; N, 4.07. Found: C, 55.91; H, 6.40; N, 4.01.

5'-Fluoro-1',2'-dimethylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2j**).

4-Fluorophenylhydrazine hydrochloride was reacted with 1-cyclohexylethanone to give 5'-fluoro-2'-methylspiro[cyclohexane-1,3'-indole] (yield 85%), which was methylated to **2j**, yield 59%, mp 242-243° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.38-2.03 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.72 (s, 3H, 2'-CH$_3$), 3.92 (s, 3H, 1'-CH$_3$), 7.42-7.97 (m, 3H, arom-H).

Anal. Calcd. for C$_{15}$H$_{19}$ClFNO$_4$: C, 54.30; H, 5.77; N, 4.22. Found: C, 54.10; H, 5.80; N, 4.21.

5'-Chloro-1',2'-dimethylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2k**).

4-Chlorophenylhydrazine hydrochloride was reacted with 1-cyclohexylethanone to give 5'-chloro-2'-methylspiro[cyclohexane-1,3'-indole] (yield 88%), which was methylated to **2k**, yield 61%, mp 185-186° (dec) (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.38-2.02 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.74 (s, 3H, 2'-CH$_3$), 3.91 (s, 3H, 1'-CH$_3$)), 7.67-8.08 (m, 3H, arom-H).

Anal. Calcd. for C$_{15}$H$_{19}$Cl$_2$NO$_4$: C, 51.74; H, 5.50; N, 4.02. Found: C, 51.80; H, 5.38; N, 4.00.

5'-Bromo-1',2'-dimethylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2l**).

4-Bromophenylhydrazine hydrochloride was reacted with 1-cyclohexylethanone to give 5'-bromo-2'-methylspiro[cyclohexane-1,3'-indole] (yield 95%), which was methylated to **2l**, yield 43%, mp 305-306° (dec) (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.83-2.01 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.73 (s, 3H, 2'-CH$_3$), 3.90 (s, 3H, 1'-CH$_3$), 7.85-8.19 (m, 3H, arom-H).

Anal. Calcd. for C$_{15}$H$_{19}$BrClNO$_4$: C, 45.88; H, 4.88; N, 3.57. Found: C, 45.80; H, 4.80; N, 3.60.

5'-Iodo-1',2'-dimethylspiro[cyclohexane-1,3'-indolium] Perchlorate (**2m**).

4-Iodophenylhydrazine was reacted with 1-cyclohexylethanone to give 5'-iodo-2'-methylspiro[cyclohexane-1,3'-indole] (yield 89%), which was methylated to **2m**, yield 37%, mp 285-286° (dec) (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.37-2.02 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.71 (s, 3H, 2'-CH$_3$), 3.88 (s, 3H, 1'-CH$_3$), 7.69-8.31 (m, 3H, arom-H).

Anal. Calcd. for C$_{15}$H$_{19}$ClINO$_4$: C, 40.98; H, 4.36; N, 3.19. Found: C, 41.00; H, 4.31; N, 3.20.

2',3'-Dimethylspiro[cyclohexane-1,1'-benzo[e]indolium] Perchlorate (**5**).

2-Naphthylhydrazine was reacted with 1-cyclohexylethanone to give 2'-methylspiro[cyclohexane-1,1'-benzo[*e*]indole] (yield 96%), which was methylated to **5**, yield 47%, mp 258-259° (acetonitrile/ether); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.74-1.95 (m, 10H, 1',1'-(CH$_2$)$_5$), 2.99 (s, 3H, 2'-CH$_3$), 4.04 (s, 3H, 3'-CH$_3$), 7.65-8.35 (m, 6H, arom-H).

Anal. Calcd. for C$_{19}$H$_{22}$ClNO$_4$: C, 62.72; H, 6.03; N, 3.85. Found: C, 62.70; H, 6.00; N, 3.90.

1',2'-Dimethylspiro[cyclohexane-1,3'-benzo[g]indolium] Perchlorate (**8**).

1-Naphthylhydrazine was reacted with 1-cyclohexylethanone to give 2'-methylspiro[cyclohexane-1,3'-benzo[g]indole] (yield

96%), which was methylated to **8**, yield 5%, mp 254-255° (acetonitrile/ether); ^{1}H nmr (dimethyl-d$_6$ sulfoxide): δ 1.40-2.09 (m, 10H, 3',3'-(CH$_2$)$_5$), 2.83 (s, 3H, 3'-CH$_3$), 4.40 (s, 3H, 1'-CH$_3$), 7.61-8.73 (m, 6H, arom-H).

Anal. Calcd. for C$_{19}$H$_{22}$ClNO$_4$: C, 62.72; H, 6.09; N, 3.85. Found: C, 62.70; H, 6.15; N, 3.95.

Synthesis of the Dispiro Compounds **4**, **7** and **10** from 2,4,6-Triarylpyrylium Perchlorates **1** and Spiroindolium Perchlorates **2**, **5** and **8**.

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

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate **1**, 5 mmoles spiroindolium perchlorate **2/5/8**, triethylamine (1.51 g, 15 mmoles) and acetic acid (0.60 g, 10 mmoles) were added. The reaction mixture was then refluxed for two hours. The dispiro compounds **4/7/10** formed crystallized in some cases from the hot reaction mixture. Otherwise their crystallization was initiated by cooling. They were filtered by suction, washed with ethanol and recrystallized from ethanol/toluene.

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