Ring Transformations of Heterocyclic Compounds. **XXIV** [1]. 1',2',5',6'-Tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinoline] and 1,2,4,5,6,7-Hexahydrospiro[azepino[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]diene] – Two New Spiro[cyclohexadiene-azaheterocycles] Easily Accessible by Pyrylium Ring Transformation

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Dedicated to the memory of Mrs. Ada Castle

The ring transformation of 2,4,6-triarylpyrylium salts **1** with 2-methyleneindolines of the type **3** in which the nitrogen atom is connected with the *ortho*-carbon of the benzene ring by a $(CH_2)_n$ chain is studied. Whereas the reaction of the pyrylium salts **1** with the 2-methylene-1,2,4,5-tetrahydropyrrolo[3,2,1-*hi*]indole **3a** (n = 2), generated *in situ* from the 4-methyl-2,5-dihydro-1*H*-pyrrolo[3,2,1-*hi*]indolium perchlorate **2a**, failed, the salts **1** react with the 2-methylene-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolines **3b**,**c** (n = 3) and the 2-methylene-1,2,4,5,6,7-hexahydroazepino[3,2,1-*hi*]indole **3d** (n = 4), obtained *in situ* from the corresponding 2-methyl-1,4,5,6-tetrahydropyrrolo[3,2,1-*if*]quinolinium perchlorates **2b**,**c** and the 2-methyl-4,5,6,7-tetrahydro-1*H*-azepino[3,2,1-*hi*]indolium perchlorate **2d**, in the presence of triethylamine/acetic acid in boiling ethanol by a 2,5-[C_4+C_2] transformation in high yield and diastereoselectivity to give the 1',2',5',6'-tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinolines] **5** and the 1,2,4,5,6,7-hexahydrospiro[azepino[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]dienes] **6**, respectively. The influence of the length of the $(CH_2)_n$ chain in **3** on the product formation and the diastereoselectivity can be explained by differences of the steric strain in the spiro compounds.

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In a previous paper of this series [2] it has been reported that the ring transformation of 2,4,6-triarylpyrylium salts **1** [3] with 2-methyleneindolines [4] proceeds with high diastereoselectivity to spiro[cyclohexa-2,4-diene-1,2'-indolines] with a *trans* configuration of the more bulky substituents at the cylohexadiene moiety. These compounds are the first members of a novel class of photochromic substances, the spiro[cyclohexadieneazaheterocycles] [5]. Later, the transformation of the salts **1** could be successfully extended to chiral methyleneindolines [6], to benzo fused methyleneindolines [7] as well as to methyleneindolines *spiro* connected in position 3 with a carbocyclic or heterocyclic ring [8].

Until now in all the cases studied have the indoline nitrogen atom bearing only an alkyl or aryl substituent allowing for a high conformationally flexibility of the molecule. The connection of the nitrogen with the *ortho* C-atom of the benzene ring by a small saturated carbon chain $(CH_2)_n$ as it is present in the 2-methylene-1,2,4,5-tetrahydropyrrolo[3,2,1-*hi*]indole **3a** (n = 2), in the 2-methylene-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolines **3b**,**c** (n = 3) and in the 2-methylene-1,2,4,5,6,7-hexahydroazepino[3,2,1-*hi*]indole **3d** (n = 4), leads to a more rigid environment which should have some influence on the course of the pyrylium ring transformation and/or on the structure of the products obtained. In this paper we wish to report on the results of such investigations.

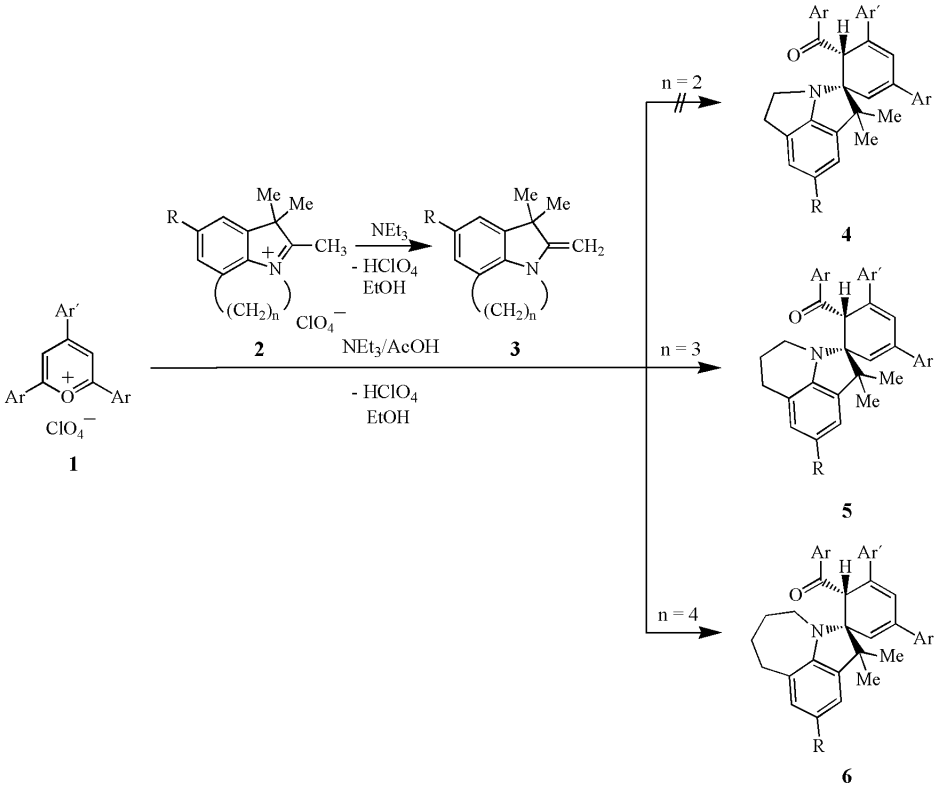
When 2,4,6-triarylpyrylium salts **1** were treated with the 2-methylene-1,2,4,5-tetrahydropyrrolo[3,2,1-*hi*]indole **3a**, generated *in situ* from the corresponding 4-methyl-2,5-dihydro-1*H*-pyrrolo[3,2,1-*hi*]indolium perchlorate **2a**, and triethylamine/acetic acid in boiling ethanol, no ring transformation product of the type **4** was obtained [9]. Changing triethylamine by other bases, such as sodium acetate, piperidine acetate or sodium ethoxide, successfully used for related pyrylium transformations [3], gave the same result. Obviously, the two fused five membered rings and the *spiro* connected cyclohexadiene moiety present in **4** make the molecule sterically overcrowded to such an extent that its formation is not observed.

Incorporating the nitrogen in one five- and one six-membered ring instead in two five-membered rings as it is the case in the 2-methylene-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolines **3b**,**c** reduces the steric strain and makes the ring transformation with the 2,4,6-triarylpyrylium salts **1** possible. When the pyrylium salts **1a-e** and the methylenequinolines **3b**,**c**, generated *in situ* from the corresponding 2-methyl-1,4,5,6-tetrahydropyrrolo[3,2,1-*if*]quinolinium perchlorates **2b**,**c** by deprotonation, were refluxed with triethylamine/acetic acid in ethanol the 1',2',5',6'-tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinolines] **5a-f** were obtained in 76-96% yield [9]. The nmr analysis of the transformation products showed that, by a very large margin, the major product is the diastereomer in which the more bulky substituents (ArCO and CMe_2) at the cyclohexadiene ring have a *trans* configuration was formed as a racemate. Traces of the other possible diastereomer (*cis*-ArCO, CMe_2), detectable by nmr spectroscopy in the crude products, could easily be removed by recrystallization.

Concerning the mechanism of the transformation one may assume that the methylenequinolines **3b**,**c** act as carbon nucleophiles of the enamine type which attack the cation of **1** at the preferred position 2 [3]. Then by ring opening/ring closure a cyclohexadiene ring is formed [10]. Since it contains four carbon atoms of the pyrylium cation and two C-atoms of the methylene derivative, connecting the former positions 2 and 5 of **1**, the transformation can be classified as a 2,5-[C_4+C_2] reaction [11].

The ring transformation also worked well with the 2-methylene-1,2,4,5,6,7-hexahydroazepino[3,2,1-*hi*]indole **3d** in which the nitrogen atom is part of a five- and a seven-membered ring. When the 2,4,6-triarylpyrylium salts **1a**-**h** were reacted with the methyleneindole **3d**, formed *in situ* from the corresponding 2-methyl-4,5,6,7-tetrahydro-1*H*-azepino[3,2,1-*hi*]indolium perchlorate **2d**, the 1,2,4,5,6,7-hexahydrospiro[azepino[3,2-*hi*]indole-2,1'-cyclohexa[2,4]dienes] **6a**-**h** were obtained by the same 2,5-[C_4+C_2] transformation [11] (yield 83-94%) [9]. The nmr analysis of the products indicated that i) the racemic diastereomer with a *trans* configuration of ArCO and CMe_2 was formed and ii) the crude products did not contain any traces of the other possible diastereomer.

The investigations clearly show that for a successful and high diastereoselective pyrylium ring transformation the nitrogen atom should be incorporated in a molecule with sufficient conformationally flexibility, *i.e.* without too much steric strain. This prerequisite is fulfilled if the N-atom is part of a five- and a six-membered, or better of a five- and a seven-membered ring, but not in two five-membered rings.



1	2/3	Ar	Ar'	n	R	5	6
a	**b**	Ph	Ph	3	H	**a**	
b	**b**	Ph	4-Me-C_6H_4	3	H	**b**	
c	**b**	Ph	4-Cl-C_6H_4	3	H	**c**	
d	**b**	Ph	4-Br-C_6H_4	3	H	**d**	
e	**b**	Ph	4-O_2N-C_6H_4	3	H	**e**	
a	**c**	Ph	Ph	3	Me	**f**	
a	**d**	Ph	Ph	4	H		**a**
b	**d**	Ph	4-Me-C_6H_4	4	H		**b**
c	**d**	Ph	4-Cl-C_6H_4	4	H		**c**
d	**d**	Ph	4-Br-C_6H_4	4	H		**d**
e	**d**	Ph	4-O_2N-C_6H_4	4	H		**e**
f	**d**	4-Me-C_6H_4	Ph	4	H		**f**
g	**d**	4-Cl-C_6H_4	Ph	4	H		**g**
h	**d**	4-Br-C_6H_4	Ph	4	H		**h**

Figure 1

Table 1

Physical and Analytical Data for the 1',2',5',6'-Tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinolines] **5** and the 1,2,4,5,6,7-Hexahydrospiro[azepino[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]dienes] **6**

No.	Compound	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N
5a	6-Benzoyl-1',1'-dimethyl-3,5-diphenyl-1',2',5',6'-tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinoline]	79	157-159	$C_{37}H_{33}NO$ (507.7)	87.54 87.30	6.55 6.61	2.76 2.70
5b	6-Benzoyl-1',1'-dimethyl-5-(4-methylphenyl-3-phenyl-1',2',5',6'-tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinoline]	76	146-147	$C_{38}H_{35}NO$ (521.7)	87.49 87.50	6.76 6.71	2.68 2.61
5c	6-Benzoyl-5-(4-chlorophenyl)-1,1'-dimethyl-3-phenyl-1',2',5',6'-tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinoline]	90	192-193	$C_{37}H_{32}ClNO$ (542.1)	81.98 81.97	5.95 5.91	2.58 2.62
5d	6-Benzoyl-5-(4-bromophenyl)-1',1'-dimethyl-3-phenyl-1',2',5',6'-tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinoline]	96	194-195	$C_{37}H_{32}BrNO$ (586.6)	75.76 75.71	5.50 5.59	2.39 2.41
5e	6-Benzoyl-1',1'-dimethyl-5-(4-nitrophenyl)-5-phenyl-1',2',5',6'-tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinoline]	89	223-224	$C_{37}H_{32}ClN_2O_3$ (552.7)	80.41 80.39	5.84 5.87	5.07 5.15
5f	6-Benzoyl-1',1',8'-trimethyl-3,5-diphenyl-1',2',5',6'-tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinoline]	84	174-176	$C_{38}H_{35}NO$ (521.7)	87.49 87.52	6.76 6.71	2.68 2.75
6a	6'-Benzoyl-1,1-dimethyl-3',5'-diphenyl-1,2,4,5,6,7-hexahydrospiro[azepino[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]diene]	90	207-208	$C_{38}H_{35}NO$ (521.7)	87.49 87.53	6.76 6.82	2.68 2.57
6b	6'-Benzoyl-1,1-dimethyl-5-(4-methylphenyl)-3-phenyl-1,2,4,5,6,7- hexahydrospiro[azepino-[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]diene]	81	151-153	$C_{39}H_{37}NO$ (535.7)	87.44 87.38	6.96 7.00	2.61 2.68
6c	6'-Benzoyl-5'-(4-chlorophenyl)-1,1-dimethyl-3-phenyl-1,2,4,5,6,7-hexahydrospiro[azepino [3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]diene]	94	208-209	$C_{38}H_{34}ClNO$ (556.2)	82.07 82.10	6.16 6.25	2.52 2.60
6d	6'-Benzoyl-5'-(4-bromophenyl)-1,1-dimethyl-3-phenyl-1,2,4,5,6,7- hexahydrospiro[azepino-[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]diene]	89	203-204	$C_{38}H_{34}BrNO$ (600.6)	75.99 76.02	5.71 5.75	2.33 2.36
6e	6'-Benzoyl-1,1-dimethyl-5-(4-nitrophenyl)-3-phenyl-1,2,4,5,6,7-hexahydrospiro[azepino-[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]diene]	83	218-219	$C_{38}H_{34}N_2O_3$ (566.7)	80.54 80.48	6.05 6.10	4.94 5.00
6f	1,1-Dimethyl-6'-(4-methylbenzoyl)-3-(4-methylphenyl)-5-phenyl-1,2,4,5,6,7-hexahydrospiro-[azepino[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]diene]	87	179-180	$C_{40}H_{39}NO$ (549.8)	87.39 87.43	7.15 7.20	2.55 2.60
6g	6'-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-1,1-dimethyl-5-phenyl-1,2,4,5,6,7-hexahydrospiro[azepino[3,2,1-*hi*]indole-2,1'-cylohexa[2,4]diene]	91	195-196	$C_{38}H_{33}Cl_2NO$ (590.6)	77.28 77.30	5.63 5.68	2.37 2.32
6h	6'-(4-Bromobenzoyl)-3-(4-bromophenyl)-1,1-dimethyl-5-phenyl-1,2,4,5,6,7-hexahydrospiro-[azepino[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]diene]	88	196-197	$C_{38}H_{33}Br_2NO$ (679.5)	67.17 67.20	4.90 4.99	2.06 2.11

The results of the elemental analyses and the spectroscopic data confirm the structure of the spiro compounds **5a**-**f** and **6 a**-**h** (*cf.* Tables 1 and 2). In the ^{1}H nmr spectra the geminal methyl groups cause two singlets (**5 a**-**f**: 1.21-1.27 ppm, 1.39-1.46 ppm; **6 a**-**h**: 1.08-1.11 ppm, 1.31-1.34 ppm) since they are diastereotopic by nature. For the same reason each hydrogen atom of the saturated carbon chain connecting the nitrogen with the *ortho*-carbon gives rise to its own signal, which was assigned by a careful analysis of the COSY and HMQC spectra. The methine hydrogen is responsible for a singlet at 5.04-5.30 ppm. NOE experiments showed that this hydrogen atom is located near one of the methyl groups indicating that the more bulky substituents at the cyclohexadiene moiety (ArCO and CMe_2) have, as in comparable spiro[cyclohexadiene-azaheterocycles] [2,6-8], a *trans* configuration. The olefinic cyclohexadiene hydrogen at C-2 of **5 a**-**f** and C-2' of **6a**-**h** resonates as a singlet at 5.85-5.93 ppm and 6.06-6.22 ppm, respectively. Another singlet found at 6.63-6.91 ppm in the region of the multiplet of the protons bonded at the benzene rings (6.48-8.02 ppm) can be attributed to the second olefinic cyclohexadiene hydrogen at C-4 of **5 a**-**f**/C-4' of **6 a**-**h**.

The presence of the carbonyl group is documented by a strong C=O-vibration band at 1676-1680 cm^{-1} and, as the

Table 2

Spectral Data for the 1',2',5',6'-Tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinolines] **5** and the 1,2,4,5,6,7-Hexahydropiro[azepino[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]-dienes] **6**

Compound	IR (KBr) ν (cm^{-1}) C=O	UV (CH_3CN) λ_{max} (nm) (log ε)	^{1}H-NMR (deuteriochloroform) [a] δ (ppm)
5a [b],[c]	1680	254 (4.62), 313 (4.06)	1.22 (s, 3H, 1'-CH_3), 1.27 (m, 1H, 5'-H), 1.42 (s, 3H, 1'-CH_3), 1.46 (m, 1H, 5'-H), 1.72 (m, 1H, 6'-H), 2.27 (m, 1H, 6'-H), 2.65 (m, 1H, 4'-H), 3.05 (m, 1H, 4'-H), 5.30 (s, 1H, 6-H), 5.86 (s, 1H, 2-H), 6.89 (s, 1H, 4-H), 6.50-7.86 (m, 18H, arom-H)
5b	1678	256 (4.64), 315 (4.12)	1.22 (s, 3H, 1'-CH_3), 1.31 (m, 1H, 5'-H), 1.42 (s, 3H, 1'-CH_3), 1.47 (m, 1H, 5'-H), 1.74 (m, 1H, 6'-H), 2.17 (s, 3H, 5-C*H*$_3$C$_6$H$_4$), 2.29 (m, 1H, 6'-H), 2.65 (m, 1H, 4'-H), 3.07 (m, 1H, 4'-H), 5.29 (s, 1H, 6-H), 5.85 (s, 1H, 2-H), 6.87 (s, 1H, 4-H), 6.51-7.86 (m, 17H, arom-H)
5c	1678	256 (4.64), 315 (4.13)	1.21 (s, 3H, 1'-CH_3), 1.29 (m, 1H, 5'-H), 1.40 (s, 3H, 1'-CH_3), 1.44 (m, 1H, 5'-H), 1.73 (m, 1H, 6'-H), 2.28 (m, 1H, 6'-H), 2.64 (m, 1H, 4'-H), 3.06 (m, 1H, 4'-H), 5.24 (s, 1H, 6-H), 5.88 (s, 1H, 2-H), 6.87 (s, 1H, 4-H), 6.48-7.83 (m, 17H, arom-H)
5d	1678	256 (4.62), 317 (4.13)	1.21 (s, 3H, 1'-CH_3), 1.28 (m, 1H, 5'-H), 1.39 (s, 3H, 1'-CH_3), 1.44 (m, 1H, 5'-H), 1.71 (m, 1H, 6'-H), 2.27 (m, 1H, 6'-H), 2.63 (m, 1H, 4'-H), 3.06 (m, 1H, 4'-H), 5.23 (s, 1H, 6-H), 5.89 (s, 1H, 2-H), 6.88 (s, 1H, 4-H), 6.49-7.84 (m, 17H, arom-H)
5e	1680	252 (4.59), 296 sh (4.10), 368 (4.01)	1.23 (s, 3H, 1'-CH_3), 1.46 (s, 3H, 1'-CH_3), 1.95 (m, 1H, 5'-H), 2.08 (m, 1H, 5'-H), 2.54 (m, 2H, 6'-H), 2.90 (m, 1H, 4'-H), 3.11 (m, 1H, 4'-H), 5.12 (s, 1H, 6-H), 5.93 (s, 1H, 2-H), 6.63 (s, 1H, 4-H), 6.61-8.02 (m, 17H, arom-H)
5f	1680	255 (4.63), 3.17 (4.07)	1.27 (s, 3H, 1'-CH_3), 1.27 (m, 1H, 5'-H), 1.42 (s, 3H, 1'-CH_3), 1.42 (m, 1H, 5'-H), 1.87 (m, 1H, 6'-H), 2.20 (s, 3H, 8'-CH_3), 2.26 (m, 1H, 6'-H), 2.62 (m, 1H, 4'-H), 2.95 (m, 1H, 4'-H), 5.29 (s, 1H, 6-H), 5.85 (s, 1H, 2-H), 6.91 (s, 1H, 4-H), 6.55-7.97 (m, 17H, arom-H)
6a [b],[c]	1678	250 (4.58), 305 sh (4.01), 382 sh (3.46)	0.85 (m, 3H, 5-H, 6-H, 7-H), 1.10 (s, 3H, 1-CH_3), 1.34 (s, 3H, 1-CH_3), 1.45 (m, 1H, 6-H), 1.56 (m, 1H, 5-H), 2.22 (m, 1H, 7-H), 2.75 (m, 1H, 4-H), 3.56 (m, 1H, 4-H), 5.13 (s, 1H, 6'-H), 6.10 (s, 1H, 2'-H), 6.75 (s, 1H, 4'-H), 6.74-7.59 (m, 18H, arom-H)
6b	1678	249 (4.55), 309 (4.04), 388 sh (3.50)	0.85 (m, 3H, 5-H, 6-H, 7-H), 1.09 (s, 3H, 1-CH_3), 1.33 (s, 3H, 1-CH_3), 1.43 (m, 1H, 6-H), 1.54 (m, 1H, 5-H), 2.12 (s, 3H, 5'-C*H*$_3$C$_6$H$_4$), 2.21 (m, 1H, 7-H), 2.73 (m, 1H, 4-H), 3.56 (m, 1H, 4-H), 5.13 (s, 1H, 6'-H), 6.08 (s, 1H, 2'-H), 6.76 (s, 1H, 4'-H), 6.73-7.59 (m, 17H, arom-H)
6c	1678	252 (4.61), 309 (4.09), 394 sh (3.53)	0.85 (m, 3H, 5-H, 6-H, 7-H), 1.10 (s, 3H, 1-CH_3), 1.31 (s, 3H, 1-CH_3), 1.45 (m, 1H, 6-H), 1.55 (m, 1H, 5-H), 2.22 (m, 1H, 7-H), 2.75 (m, 1H, 4-H), 3.55 (m, 1H, 4-H), 5.08 (s, 1H, 6'-H), 6.12 (s, 1H, 2'-H), 6.77 (s, 1H, 4'-H), 6.74-7.59 (m, 17H, arom-H)
6d	1678	252 (4.58), 309 (4.07), 394 sh (3.53)	0.89 (m, 3H, 5-H, 6-H, 7-H), 1.09 (s, 3H, 1-CH_3), 1.31 (s, 3H, 1-CH_3), 1.44 (m, 1H, 6-H), 1.56 (m, 1H, 5-H), 2.22 (m, 1H, 7-H), 2.74 (m, 1H, 4-H), 3.54 (m, 1H, 4-H), 5.07 (s, 1H, 6'-H), 6.12 (s, 1H, 2'-H), 6.76 (s, 1H, 4'-H), 6.74-7.59 (m, 17H, arom-H)
6e	1676	250 (4.51), 294 sh (4.09), 373 (3.97)	0.85 (m, 3-H, 5-H, 6-H, 7-H), 1.11 (s, 3H, 1-CH_3), 1.31 (s, 3H, 1-CH_3), 1.45 (m, 1H, 6-H), 1.57 (m, 1H, 5-H), 2.23 (m, 1H, 7-H), 2.77 (m, 1H, 4-H), 3.54 (m, 1H, 4-H), 5.12 (s, 1H, 6'-H), 6.22 (s, 1H, 2'-H), 6.77 (s, 1H, 4'-H), 6.75-7.93 (m, 17H, arom-H)
6f		261 (4.65), 311 sh (3.99), 391 sh (3.46)	0.87 (m, 3H, 3-H, 5-H, 7-H), 1.08 (s, 3H, 1-CH_3), 1.32 (s, 3H, 1-CH_3), 1.45 (m, 1H, 6-H), 1.52 (m, 1H, 5-H), 2.21 (m, 1H, 7-H), 2.26 (s, 3H, 3'-C*H*$_3$C$_6$H$_4$), 2.30 (s, 3H, 6'-C*H*$_3$C$_6$H$_4$), 2.74 (m, 1H, 4-H), 3.56 (m, 1H, 4-H), 5.08 (s, 1H, 6'-H), 6.06 (s, 1H, 2'-H), 6.74 (s, 1H, 4'-H), 6.70-7.49 (m, 16H, arom-H)
6g	1678	259 (4.65), 311 sh (3.97), 388 sh (3.38)	0.88 (m, 3H, 5-H, 6-H, 7-H), 1.08 (s, 3H, 1-CH_3), 1.32 (s, 3H, 1-CH_3), 1.49 (m, 1H, 6-H), 1.58 (m, 1H, 5-H), 2.29 (m, 1H, 7-H), 2.75 (m, 1H, 4-H), 3.52 (m, 1H, 4-H), 5.05 (s, 1H, 6'-H), 6.07 (s, 1H, 2'-H), 6.71 (s, 1H, 4'-H), 6.72-7.51 (m, 16H, arom-H)
6h	1678	262 (4.75), 313 sh (4.03), 394 sh (3.46)	0.88 (m, 3H, 5-H, 6-H, 7-H), 1.08 (s, 3H, 1-CH_3), 1.32 (s, 3H, 1-CH_3), 1.50 (m, 1H, 6-H), 1.59 (m, 1H, 5-H), 2.32 (m, 1H, 7-H), 2.75 (m, 1H, 4-H), 3.51 (m, 1H, 4-H), 5.04 (s, 1H, 6'-H), 6.08 (s, 1H, 2'-H), 6.70 (s, 1H, 4'-H), 6.71-7.50 (m, 16H, arom-H)

[a] X-/x'-H denotes the protons in x-/x'-position and arom-H the protons bonded to the benzene rings of **5** and **6**; [b] ^{13}C nmr (deuteriochloroform) **5a** 20.5 (C-6'), 22.2 (C-5'), 22.3 (1-CH_3), 23.5 (1-CH_3), 41.3 (C-4'), 45.0 (C-6), 51.6 (C-1'), 76.7 (*spiro*-C), 115.2, 117.2, 117.8, 121.5, 122.9, 123.1, 124.0, 124.6, 125.7, 126.4, 126.6, 126.7, 126.8, 131.0, 132.6, 135.6, 135.9, 136.9, 137.7, 138.1, 143.8 (olefinic and aromatic carbons), 195.7 (CO), **6a** 18.5 (1-CH_3), 25.1 (C-6), 27.3 (1-CH_3), 28.6 (C-5), 33.3 (C-7), 45.0 (6'-C), 48.5 (C-4), 51.9 (C-1), 76.3 (*spiro*-C), 118.1, 119.6, 122.1, 123.4, 124.2, 125.6, 126.2, 126.3, 126.5, 126.6, 127.1, 127.2, 130.3, 135.4, 135.9, 136.0, 137.1, 137.8, 138.8, 146.5 (olefinic and aromatic carbons), 194.3 (CO); [c] Mass spectra m/z (%) **5a** 507 (23) [M$^+$], 401 (100), 305 (67), 105 (66) [PhCO$^+$], 91 (42), 77 (14) [Ph$^+$], **6a** 521 (100) [M$^+$], 418 (75), 324 (28), 105 (54) [PhCO$^+$], 91 (70), 77 (36) [Ph$^+$].

^{13}C nmr spectra of **5a** and **6a** show, by its typical carbon resonance around 200 ppm.

A characteristic feature of the uv spectra is an intense absorption at 249-262 nm usually accompanied by another band of lower intensity (**5a**-**f**) or two shoulders (**6a**-**h**) at longer wavelengths.

EXPERIMENTAL

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 at 25° with hexamethyl

disiloxane as internal standard, ir spectra were obtained on a ATI Mattson Genesis FTIR spectrophotometer (in potassium bromide) and uv spectra on a Zeiss M 40 instrument (acetonitrile, 25°). Mass spectra were determined on a Finnigan MAT 111 A spectrometer (70 eV, electron impact). The pyrylium perchlorates **1a** [12], **1b** [13], **1c**,**e** [14], **1d** [15], **1f**-**h** [16] were synthesized according to literature procedures. For the preparation of the indolium perchlorates **2a**,**d** and the quinolinium perchlorates **2b**,**c** a recently developed one-pot procedure was used [17].

Synthesis of 1',2',5',6'-Tetrahydro-4'*H*-spiro[cyclohexa-2,4-diene-1,2'-pyrrolo[3,2,1-*ij*]quinolines] **5** and 1,2,4,5,6,7-Hexahydrospiro[azepino[3,2,1-*hi*]indole-2,1'-cyclohexa[2,4]dienes] **6** from 2,4,6-Triarylpyrylium Perchlorates **1**, 1,4,5,6-Tetrahydropyrrolo-[3,2,1-*ij*]quinolinium Perchlorates **2b**,**c** and 4,5,6,7-Tetrahydro-1*H*-azepino[3,2,1-*hi*]indolium Perchlorate **2d**.

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

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate **1**, 5 mmoles quinolinium perchlorate **2b**,**c** and indolium perchlorate **2d**, respectively, 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 spiro compounds **5**/**6** formed crystallized in most cases from the hot reaction mixture. Otherwise their crystallization was initiated by cooling. The products were collected by suction filtration, washed with ethanol and recrystallized from ethanol/toluene.

If the pyrylium salt **1a** was reacted with the 4-methyl-2,5-dihydro-1*H*-pyrrolo[3,2,1-*hi*]indolium perchlorate **2a** under these conditions no transformation product of the type **4** was obtained.

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