

Table 1

Physical and Analytical Data for the 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-2',3'-dihydro-1'*H*-benzo[*e*]indoles] **6** and benzo[*g*]indoles] **7**

No.	-spiro[cyclohexa-2,4-diene-1,2'-2',3'-dihydro-1' <i>H</i> -benzo[<i>x</i>]indole] [<i>a</i>]	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%)		
					Calcd./Found	C	H
6a	6-Benzoyl-1',1',3',3'-trimethyl-3,5-diphenyl-	89	177-178	C ₃₉ H ₃₃ NO (531.7)	88.10 88.08	6.26 6.23	2.63 2.65
6b	6-Benzoyl-1',1',3',3'-trimethyl-5-(4-methylphenyl)-3-phenyl-	92	192-193	C ₄₀ H ₃₅ NO (545.7)	88.04 88.09	6.46 6.41	2.57 2.50
6c	6-Benzoyl-5-(4-methoxyphenyl)-1',1',3'-trimethyl-3-phenyl-	62	197-198	C ₄₀ H ₃₅ NO ₂ (561.7)	85.53 85.60	6.28 6.33	2.49 2.54
6d	6-Benzoyl-5-(4-chlorophenyl)-1',1',3'-trimethyl-3-phenyl-	87	197-198	C ₃₉ H ₃₂ ClNO (566.1)	82.74 82.80	5.70 5.73	2.47 2.41
6e	6-Benzoyl-5-(4-bromophenyl)-1',1',3'-trimethyl-3-phenyl-	93	193-194	C ₃₉ H ₃₂ BrNO (610.6)	76.72 76.80	5.28 5.21	2.29 2.21
6f	6-Benzoyl-1',1',3',3'-trimethyl-5-(4-nitrophenyl)-3-phenyl-	71	229-230	C ₃₉ H ₃₂ N ₂ O ₃ (576.7)	81.23 81.20	5.59 5.63	4.86 4.90
6g	1',1',3',3'-Trimethyl-6-(4-methylbenzoyl)-3-(4-methylphenyl)-5-phenyl-	87	224-225	C ₄₁ H ₃₇ NO (559.8)	87.98 87.93	6.66 6.60	2.50 2.41
6h	6-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-1',1',3'-trimethyl-5-phenyl-	93	221-222	C ₃₉ H ₃₁ Cl ₂ NO (600.6)	78.00 78.10	5.20 5.28	2.33 2.30
6i	6-(4-Bromobenzoyl)-3-(4-bromophenyl)-1',1',3'-trimethyl-5-phenyl-	87	210-211	C ₃₉ H ₃₁ Br ₂ NO (689.5)	67.94 67.90	4.53 4.60	2.03 2.10
6j	6-Benzoyl-3'-ethyl-1',1'-dimethyl-3,5-diphenyl-	81	174-175	C ₄₀ H ₃₅ NO (545.7)	88.04 88.11	6.46 6.52	2.57 2.60
7a	6-Benzoyl-1',3',3'-trimethyl-3,5-diphenyl-	78	203-204	C ₃₉ H ₃₃ NO (531.7)	88.10 88.11	6.26 6.30	2.63 2.59
7b	6-Benzoyl-1',3',3'-trimethyl-5-(4-methylphenyl)-3-phenyl-	76	192-193	C ₄₀ H ₃₅ NO (545.7)	88.04 88.00	6.46 6.41	2.57 2.59
7c	6-Benzoyl-1',3',3'-trimethyl-5-(4-methoxyphenyl)-3-phenyl-	83	183-184	C ₄₀ H ₃₅ NO ₂ (561.7)	85.53 85.60	6.28 6.35	2.49 2.55
7d	6-Benzoyl-5-(4-chlorophenyl)-1',3',3'-trimethyl-3-phenyl-	78	221-222	C ₃₉ H ₃₂ ClNO (566.1)	82.74 82.71	5.70 5.72	2.47 2.51
7e	6-Benzoyl-5-(4-bromophenyl)-1',3',3'-trimethyl-3-phenyl-	76	224-225	C ₃₉ H ₃₂ BrNO (610.6)	76.72 76.80	5.28 5.30	2.29 2.30
7f	6-Benzoyl-1',3',3'-trimethyl-5-(4-nitrophenyl)-3-phenyl-	71	235-236	C ₃₉ H ₃₂ N ₂ O ₃ (576.7)	81.23 81.30	5.59 5.48	4.86 4.79
7g	1',3',3'-Trimethyl-6-(4-methylbenzoyl)-3-(4-methylphenyl)-5-phenyl-	78	234-235	C ₄₁ H ₃₇ NO (559.8)	87.98 87.93	6.66 6.62	2.50 2.42
7h	6-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-1',3',3'-trimethyl-5-phenyl-	85	209-210	C ₃₉ H ₃₁ Cl ₂ NO (600.6)	78.00 78.10	5.20 5.23	2.33 2.40
7i	6-(4-Bromobenzoyl)-3-(4-bromophenyl)-1',3',3'-trimethyl-5-phenyl-	83	223-224	C ₃₉ H ₃₁ Br ₂ NO (689.5)	67.94 67.91	4.53 4.55	2.03 2.10

[a] **6a-j**: x = e, **7a-i**: x = g.

eneindolines, used as such or generated *in situ* from the corresponding 3*H*-indolium precursors, proceeds with high diastereoselectivity to give diastereomeric pure spiro[cyclohexadiene-indolines] having two or three stereocenters in high yield [5,7]. To get more information on the influence of structural variations of these indolines on their photochromism, *i.e.* the photochemical ring opening to coloured merocyanines and the recyclization of these by light or heat to the starting compounds, we became interested in the synthesis of spiro[cyclohexadiene-indolines] with an additional fused benzene ring at the indoline moiety. These derivatives should be available by ring transformation of the pyrylium salts **1** with benzene fused methyleneindolines. In this paper we wish to report on the results of such investigations.

When the 2,4,6-triarylpyrylium perchlorates **1a-i** and the 2-methylene-2,3-dihydro-1*H*-benzo[*e*]indoles **3a,b**, generated *in situ* from the corresponding 2-methyl-1*H*-benzo[*e*]indolium perchlorates **2a,b**, were refluxed in ethanol in the presence of triethylamine/acetic acid the envisaged 6-aryloxy-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-2',3'-dihydro-1'*H*-benzo[*e*]indoles] **6a-j** were obtained in 62-93% yield [8,9]. Under the same conditions the pyrylium salts **1a-i** react with 2-methylene-2,3-dihydro-1*H*-benzo[*g*]indole **5**, also generated *in situ* from the corresponding 2-methyl-3*H*-benzo[*g*]indolium perchlorate **4**, to give the isomeric 6-aryloxy-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-2',3'-dihydro-1'*H*-benzo[*g*]indoles] **7a-i** (yield 71-85%) [8,9] (*cf.* Tables 1 and 2). Both types of compounds represent benzo-fused

Table 2
Spectral Data for the 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-2',3'-dihydro-1'*H*-benzo[*e*]indoles] 6 and -benzo[*g*]indoles] 7

Compound	IR (KBr)	UV (CH ₃ CN)	¹ H-NMR (deuteriochloroform) [a]
	(cm ⁻¹)	λ _{max} (nm) (log ε)	δ (ppm)
6a [b],[c]	1679	256 (4.82), 303 (4.19), 314 (4.25), 397 sh (3.59)	1.24 (s, 3H, 1'-CH ₃), 1.84 (s, 3H, 1'-CH ₃), 2.57 (s, 3H, 3'-CH ₃), 5.54 (s, 1H, 6-H), 5.96 (d, 1H, 4'-H), 5.98 (s, 1H, 2-H), 6.84 (s, 1H, 4-H), 7.01-7.89 (m, 20H, arom-H)
6b	1680	257 (4.83), 303 (4.23), 314 (4.30), 391 sh (3.65)	1.23 (s, 3H, 1'-CH ₃), 1.84 (s, 3H, 1'-CH ₃), 2.06 (s, 3H, 5-C ₆ H ₄ CH ₃), 2.56 (s, 3H, 3'-CH ₃), 5.54 (s, 1H, 6-H), 5.96 (d, 1H, 4'-H), 5.96 (s, 1H, 2-H), 6.82 (s, 1H, 4-H), 6.80-7.89 (m, 19H, arom-H)
6c	1680	255 (4.82), 303 (4.25), 314 (4.32), 400 sh (3.68)	1.24 (s, 3H, 1'-CH ₃), 1.84 (s, 3H, 1'-CH ₃), 2.57 (s, 3H, 3'-CH ₃), 3.53 (s, 3H, 5-C ₆ H ₄ OCH ₃), 5.52 (s, 1H, 6-H), 5.94 (s, 1H, 2-H), 5.98 (d, 1H, 4'-H), 6.76 (s, 1H, 4-H), 6.55-7.90 (m, 19H, arom-H)
6d	1679	256 (4.85), 303 (4.24), 314 (4.30), 400 sh (3.62)	1.24 (s, 3H, 1'-CH ₃), 1.82 (s, 3H, 1'-CH ₃), 2.57 (s, 3H, 3'-CH ₃), 5.48 (s, 1H, 6-H), 5.97 (d, 1H, 4'-H), 6.00 (s, 1H, 2-H), 6.82 (s, 1H, 4-H), 6.97-7.89 (m, 19H, arom-H)
6e	1679	256 (4.84), 302 (4.24), 314 (4.30), 400 sh (3.64)	1.23 (s, 3H, 1'-CH ₃), 1.81 (s, 3H, 1'-CH ₃), 2.57 (s, 3H, 3'-CH ₃), 5.48 (s, 1H, 6-H), 5.97 (d, 1H, 4'-H), 6.00 (s, 1H, 2-H), 6.83 (s, 1H, 4-H), 7.02-7.88 (m, 19H, arom-H)
6f	1677	255 (4.80), 288 sh (4.23), 300 (4.25), 313 (4.24), 376 (4.14)	1.26 (s, 3H, 1'-CH ₃), 1.81 (s, 3H, 1'-CH ₃), 2.60 (s, 3H, 3'-CH ₃), 5.52 (s, 1H, 6-H), 6.01 (d, 1H, 4'-H), 6.11 (s, 1H, 2-H), 7.01 (s, 1H, 4-H), 7.05-7.93 (m, 19H, arom-H)
6g	1677	258 (4.85), 303 (4.16), 314 (4.23), 400 sh (3.55)	1.24 (s, 3H, 1'-CH ₃), 1.83 (s, 3H, 1'-CH ₃), 2.17 (s, 3H, 3-C ₆ H ₄ CH ₃), 2.32 (s, 3H, 6-COC ₆ H ₄ CH ₃), 2.58 (s, 3H, 3'-CH ₃), 5.48 (s, 1H, 6-H), 5.95 (s, 1H, 2H), 6.05 (d, 1H, 4'-H), 6.83 (s, 1H, 4-H), 6.86-7.90 (m, 18H, arom-H)
6h	1678	258 (4.89), 303 (4.21), 314 (4.25), 400 sh (3.62)	1.23 (s, 3H, 1'-CH ₃), 1.83 (s, 3H, 1'-CH ₃), 2.59 (s, 3H, 3'-CH ₃), 5.46 (s, 1H, 6-H), 5.96 (s, 1H, 2-H), 6.05 (d, 1H, 4'-H), 6.77 (s, 1H, 4-H), 7.04-7.89 (m, 18H, arom-H)
6i	1679	258 (4.91), 303 (4.22), 314 (4.25), 394 sh (3.62)	1.23 (s, 3H, 1'-CH ₃), 1.82 (s, 3H, 1'-CH ₃), 2.58 (s, 3H, 3'-CH ₃), 5.45 (s, 1H, 6-H), 5.97 (s, 1H, 2-H), 6.05 (d, 1H, 4'-H), 6.76 (s, 1H, 4-H), 7.06-7.89 (m, 18H, arom-H)
6j	1680	257 (4.78), 304 (4.18), 315 (4.27), 403 sh (3.57)	0.92 (t, 3H, 3'-CH ₂ CH ₃), 1.24 (s, 3H, 1'-CH ₃), 1.84 (s, 3H, 1'-CH ₃), 2.67 (m, 1H, 3'-CH ₂ CH ₃), 3.11 (m, 1H, 3'-CH ₂ CH ₃), 5.55 (s, 1H, 6-H), 5.88 (d, 1H, 4'-H), 5.96 (s, 1H, 2-H), 6.84 (s, 1H, 4-H), 6.87-7.89 (m, 20H, arom-H)
7a [b],[c]	1677	256 (4.67), 324 (4.02), 347 sh (4.00)	1.17 (s, 3H, 3'-CH ₃), 1.42 (s, 3H, 3'-CH ₃), 3.06 (s, 3H, 1'-CH ₃), 5.26 (s, 1H, 6-H), 6.16 (s, 1H, 2-H), 6.83 (s, 1H, 4-H), 6.70-7.65 (m, 21H, arom-H)
7b	1677	254 (4.65), 326 (4.06), 351 sh (4.01)	1.17 (s, 3H, 3'-CH ₃), 1.41 (s, 3H, 3'-CH ₃), 2.12 (s, 3H, 5-C ₆ H ₄ CH ₃), 3.06 (s, 3H, 1'-CH ₃), 5.26 (s, 1H, 6-H), 6.14 (s, 1H, 2-H), 6.89 (s, 1H, 4-H), 6.71-7.65 (m, 20H, arom-H)
7c	1676	251 (4.63), 331 (4.15)	1.16 (s, 3H, 3'-CH ₃), 1.41 (s, 3H, 3'-CH ₃), 3.05 (s, 3H, 1'-CH ₃), 3.55 (s, 3H, 5-C ₆ H ₄ OCH ₃), 5.24 (s, 1H, 6-H), 6.11 (s, 1H, 2-H), 6.74 (s, 1H, 4-H), 6.56-7.64 (m, 20H, arom-H)
7d	1677	254 (4.68), 325 (4.09), 350 sh (4.04)	1.17 (s, 3H, 3'-CH ₃), 1.39 (s, 3H, 3'-CH ₃), 3.06 (s, 3H, 1'-CH ₃), 5.20 (s, 1H, 6-H), 6.18 (s, 1H, 2-H), 6.81 (s, 1H, 4-H), 6.72-7.62 (m, 20H, arom-H)
7e	1675	254 (4.67), 325 (4.11), 350 sh (4.05)	1.16 (s, 3H, 3'-CH ₃), 1.39 (s, 3H, 3'-CH ₃), 3.06 (s, 3H, 1'-CH ₃), 5.19 (s, 1H, 6-H), 6.18 (s, 1H, 2-H), 6.82 (s, 1H, 4-H), 6.72-7.66 (m, 20H, arom-H)
7f	1675	251 (4.66), 354 (4.22)	1.18 (s, 3H, 3'-CH ₃), 1.38 (s, 3H, 3'-CH ₃), 3.07 (s, 3H, 1'-CH ₃), 5.24 (s, 1H, 6-H), 6.29 (s, 1H, 2-H), 7.00 (s, 1H, 4-H), 6.68-7.93 (m, 20H, arom-H)
7g	1675	258 (4.73), 325 (4.03), 352 sh (4.01)	1.15 (s, 3H, 3'-CH ₃), 1.40 (s, 3H, 3'-CH ₃), 2.05 (s, 3H, 3-C ₆ H ₄ CH ₃), 2.33 (s, 3H, 6-COC ₆ H ₄ CH ₃), 3.07 (s, 3H, 1'-CH ₃), 5.21 (s, 1H, 6-H), 6.10 (s, 1H, 2-H), 6.82 (s, 1H, 4-H), 6.51-7.65 (m, 19H, arom-H)

Table 2 (Continued)

7h	1677	257 (4.77), 323 (4.07), 347 sh (4.03)	1.16 (s, 3H, 3'-CH ₃), 1.39 (s, 3H, 3'-CH ₃), 3.05 (s, 3H, 1'-CH ₃), 5.15 (s, 1H, 6-H), 6.14 (s, 1H, 2-H), 6.75 (s, 1H, 4-H), 6.64-7.68 (m, 19H, arom-H)
7i	1677	259 (4.75), 323 (4.03), 350 sh (3.97)	1.14 (s, 3H, 3'-CH ₃), 1.37 (s, 3H, 3'-CH ₃), 3.02 (s, 3H, 1'-CH ₃), 5.13 (s, 1H, 6-H), 6.13 (s, 1H, 2-H), 6.73 (s, 1H, 4-H), 6.61-7.66 (m, 19H, arom-H)

[a] 2-H, 4-H, 6-H and 4'-H denote the protons in 2-, 4-, 6- and 4'-position, respectively, and arom-H the protons bonded to the benzene rings. [b] ¹³C nmr (deuteriochloroform) **6a** 20.5 (1'-CH₃), 23.3 (1'-CH₃), 32.0 (3'-CH₃), 43.8 (C-6), 54.7 (C-3'), 76.3 (C-1), 108.2, 118.7, 118.8, 120.0, 122.1, 122.2, 123.5, 124.3, 124.4, 125.9, 126.0, 126.4, 126.5, 126.6, 126.7, 126.8, 127.4, 127.9, 129.7, 130.8, 134.5, 136.9, 137.2, 138.4, 138.6, 145.6 (olefinic and aromatic carbons), 195.4 (6-COPh), **7a** 18.9 (3'-CH₃), 26.5 (3'-CH₃), 35.0 (1'-CH₃), 44.5 (C-6), 51.9 (C-3'), 77.0 (C-1), 118.4, 118.8, 119.2, 120.7, 120.8, 121.8, 122.4, 123.4, 124.2, 125.6, 125.7, 125.8, 126.0, 126.3, 126.5, 126.6, 130.0, 131.2, 132.6, 134.7, 136.3, 137.0, 137.2, 138.7, 143.1 (olefinic and aromatic carbons), 194.4 (6-COPh), [c] Mass spectra: (70 eV), m/z (%) **6a** 531 (16) [M⁺], 426 (63) [M⁺-PhCO], 209 (100), 105 (42) [PhCO⁺], 77 (21) [Ph⁺], **7a** 31 (17) [M⁺], 426 (27) [M⁺-PhCO], 306 (75), 225 (61), 209 (100), 105 (28) [PhCO⁺], 77 (20) [Ph⁺].

spirodihydroindoles with a former unknown substitution pattern [10].

The formation of the transformation products **6/7** can be explained in close analogy to the related reaction of the pyrylium salts **1** with anhydrobases derived from indolium salts bearing no additional fused benzene ring [5,7]. In the initial step the anhydrobases **3/5** of **2/4** are added as carbon nucleophiles of the enamine type to the preferred position 2 of the pyrylium cation [4] to give 2H-pyran intermediates [11]. Their electrocyclic ring opening leads to merocyanines which recyclize finally by another electrocyclic process to racemic but diastereomerically pure benzo-fused spiro[cyclohexadiene-dihydroindoles] **6/7** with a *trans* configuration of the more bulky substituents (CMe₂ and ArCO) at C-1 and C-6 [12]. Since in the course of the transformation **1** + **3/5** → **6/7** a cyclohexadiene ring is built up from four carbon atoms of the pyrylium cation and two C-atoms of the methylenedihydroindole by connection of the former positions 2 and 4 of **1** by a C₂-chain the reaction can be classified as a 2,5-[C₄+C₂] ring transformation [13].

The results of elemental analyses and spectroscopic data are in agreement with the structure proposed for the benzo-fused spiro[cyclohexadiene-dihydroindoles] **6/7**. In the ¹H nmr spectra the protons of the geminal methyl groups cause the expected two singlets. The methyl group directed toward the proton at C-6 is responsible for a signal at 1.14-1.26 ppm in all compounds whereas the other one resonates in **7a-i** at 1.37-1.47 ppm and in **6a-j**, because of the deshielding effect of the adjacent benzene ring, at 1.81-1.84 ppm. In the same way the singlet of the *N*-methyl group at 2.42-2.53 ppm in **6a-i** is downfield shifted to 3.02-3.07 ppm in **7a-i**. Further singlets provide the methine hydrogen at C-6 (5.13-5.55 ppm) and the olefinic H-atoms at C-2 (5.94-6.29 ppm) and C-4 (6.73-7.01 ppm); the latter one can be localized in the region of the multiplet of the benzene protons (6.51-7.93 ppm). Finally, the doublet at 5.88-6.05 ppm in the spectra of **6a-j** can be attributed to the proton at C-4' which resonates at higher field than the other aromatic protons caused by the known shielding effect of the *ortho*-positioned RN-group (R = Me, Et) [14].

To confirm the configuration of the stereocenters at C-1 and C-6 of **6/7** nOe experiments were carried out. Irradiation into the singlet of the proton at C-6 caused an enhancement of the singlet at 1.14-1.26 ppm, *i.e.* of the signal of a C-bonded methyl group, but no change in the intensity of the singlet of the N-bonded methyl, showing the proximity of both groups and hence gave evidence for the molecular structure of the diastereomer obtained.

The carbonyl group of the benzo-fused spiro[cyclohexadiene-dihydroindoles] **6/7** is responsible for the C=O vibration band in the ir spectra at 1675-1680 cm⁻¹ [15]. A characteristic feature of the uv spectra is a strong absorption at 251-259 nm, which is more intensive for **6a-j** than for **7a-i**, accompanied by up to three further bands of lower intensity at longer wavelengths.

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ¹H nmr and ¹³C nmr spectra were recorded on a Varian Gemini 200 spectrometer (¹H: 199.975 MHz, ¹³C: 50.289 MHz) and on a Varian Gemini 2000 spectrometer (¹H: 200.041 MHz, ¹³C: 50.305 MHz) in deuteriochloroform or dimethyl-d₆ 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 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** [16], **1b** [17], **1c,e** [18], **1d** [19], **1f-h** [20] and 2,3,3-trimethyl-3H-benzo[g]indole [21] were synthesized according to literature procedures. 1,1,2-Trimethyl-1H-benzo[e]indole was purchased from Acros.

Preparation of the Benzo-fused Indolium Perchlorates **2a,b** and **4a** by Alkylation of the Corresponding Indoles.

General Procedure.

The indole (30 mmoles) was dissolved in toluene (30 ml). After addition of the dialkyl sulfate (30 mmoles) the reaction mixture was magnetically stirred at 90° for 0.5 hour. The dialkyl sulfate adduct formed as an oil was separated from the toluene layer after cooling by decantation. It was dissolved in ethanol (60 ml) and perchloric acid (70% solution in water, 4.31 g,

70 mmoles) was added dropwise under magnetic stirring. After addition of ether (30 ml) the crystalline precipitate obtained was filtered by suction and washed with ethanol and ether. The crude products were used without further purification; if necessary, they can be recrystallized from acetonitrile/ether.

1,1,2,3-Tetramethyl-1*H*-benzo[*e*]indolium Perchlorate (2a).

This compound was obtained by the general procedure from 1,1,2-trimethyl-1*H*-benzo[*e*]indole and dimethyl sulfate in 78% yield, mp 211-212° (acetonitrile/ether); ¹H nmr (dimethyl-d₆ sulfoxide): δ 1.70 (s, 6H, 1-CH₃), 2.82 (s, 3H, 2-CH₃), 4.05 (s, 3H, 3-CH₃), 7.08-8.33 (m, 6H, arom-H).

Anal. Calcd. for C₁₆H₁₈ClNO₄: C, 59.35; H, 5.60; N, 4.33. Found: C, 59.40; H, 5.63; N, 4.30.

3-Ethyl-1,1,2-trimethyl-1*H*-benzo[*e*]indolium Perchlorate (2b).

This compound was obtained according to the general procedure from 1,1,2-trimethyl-1*H*-benzo[*e*]indole and diethyl sulfate in 41% yield, mp 260-261° (acetonitrile/ether) (dec); ¹H nmr (dimethyl-d₆ sulfoxide): δ 1.46 (t, 3H, 3-CH₂CH₃), 1.71 (s, 6H, 1-CH₃), 2.88 (s, 3H, 2-CH₃), 4.57 (q, 2H, 3-CH₂CH₃), 7.63-8.34 (m, 6H, arom-H).

Anal. Calcd. for C₁₇H₂₀ClNO₄: C, 60.45; H, 5.97; N, 4.15. Found: C, 60.40; H, 5.91; N, 4.20.

1,2,3,3-Tetramethyl-3*H*-benzo[*g*]indolium Perchlorate (4a).

This compound was obtained according to the general procedure from 2,3,3-trimethyl-3*H*-benzo[*g*]indole and dimethyl sulfate in 11% yield, mp 268-269° (acetonitrile/ether) (dec); ¹H nmr (dimethyl-d₆ sulfoxide): δ 1.53 (s, 6H, 3-CH₃), 2.80 (s, 3H, 2-CH₃), 4.40 (s, 3H, 1-CH₃), 7.60-8.69 (m, 6H, arom-H).

Anal. Calcd. for C₁₆H₁₈ClNO₄: C, 59.35; H, 5.60; N, 4.33. Found: C, 49.50; H, 5.63; N, 4.30.

Synthesis of 6-Aroyl-3,5-diarylspro[cyclohexa-2,4-diene-1,2'-2',3'-dihydro-1'*H*-benzo[*e*]indoles] **6** and -benzo[*g*]indoles] **7** from 2,4,6-Triarylpyrylium Perchlorates **1** and 2-Methyl Substituted Benzo[*e*] and Benzo[*g*]indolium Perchlorates **2/4**.

General Procedure (cf. Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate **1**, 5 mmoles indolium perchlorate **2/4**, 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[cyclohexadiene-dihydroindoles] **6/7** formed crystallized in the most 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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