

Ring Transformations of Heterocyclic Compounds. XVIII [1].  
Spiro[cyclohexadiene-indolines] with Three Stereocenters from  
Pyrilium Salts and Chiral Methyleneindolines - An Example of a High  
Diastereoselective Ring Transformation

Thomas Zimmermann\*

Institut für Organische Chemie der Universität Leipzig, Permoserstraße 15, D-04303 Leipzig, Germany

Ulrich Abram

Forschungszentrum Rossendorf, Institut für Radiochemie, c/o Institut für Analytische Chemie der Universität  
Dresden, Mommsenstraße, D-01062 Dresden, Germany

Received May 17, 1999

The diastereoselective synthesis of 6-aryl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-indolines] **4** possessing three stereocenters from 2,4,6-triarylpyrilium perchlorates **1** and chiral methyleneindolines **3** (generated *in situ* by deprotonation of the corresponding 3*H*-indolium perchlorates **2**) in the presence of triethylamine/acetic acid in ethanol by a 2,5-[C<sub>4</sub>+C<sub>2</sub>] pyrylium ring transformation is reported. Structure elucidation is performed by X-ray structure determinations of the spiro[cyclohexadiene-indolines] **4a**, **4p** and **4t**. The influence of various substituents at C-3 of the methyleneindolines **3** on the stereochemistry of the transformation, mechanistic details as well as spectroscopic data of the products **4** are discussed.

*J. Heterocyclic Chem.*, **36**, 1223 (1999).

In a previous paper of this series we reported on the synthesis of 3',3'-dimethyl substituted 6-aryl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-indolines] **4** (R' = R'' = Me) [2] which represent a novel type of photochromic substances [3]. They were obtained by ring transformation of the pyrilium salts **1** [4] with the achiral 3,3-dimethyl-2-methyleneindolines **3**, R' = R'' = Me (Fischer base and derivatives thereof) [5] used as such or generated *in situ* from the corresponding 3*H*-indolium salts **2** [6]. In the course of the transformation two asymmetric carbon atoms (C-1 and C-6) are created and hence the formation of two diastereomers of the products should be possible. Nevertheless, the transformation proceeded with high diastereoselectivity, *i.e.* only the isomer with a *trans* configuration of the more bulky substituents (ArCO and CMe<sub>2</sub>) at the stereocenters C-1 and C-6 was obtained [2,7].

Continuing these investigations we became interested in reactions of the pyrilium salts **1** with racemic chiral methyleneindolines **3** (R' ≠ R''). The incorporation of an asymmetric carbon atom into **3** should lead to spiro[cyclohexadiene-indolines] **4** with an additional stereocenter at C-3' which enhances the number of possible diastereomers from two to four. In this paper we wish to report on such reactions giving special attention to the influence of the kind of the two different substituents at C-3 of the methyleneindolines **3** on the diastereoselectivity of the transformations as well as on the structure of the products obtained.

The investigations were started with the methyleneindolines **3a-e** bearing a methyl and an alkyl (Et, *n*-Pr, *i*-Pr) substituent at C-3. When the 2,4,6-triarylpyrilium salts **1a-h** were reacted in the presence of triethylamine/acetic

acid in boiling ethanol with these indolines, generated *in situ* by deprotonation of the related 3*H*-indolium perchlorates **2a-e**, the spiro[cyclohexadiene-indolines] **4a-l** were obtained in 63-90% yield (*cf.* Tables 1 and 2). The analysis of the transformation products showed that from the four possible racemic diastereomers only one isomer was formed. As in the case of the 3',3'-dimethyl substituted spiro[cyclohexadieneindolines] **4** (R' = R'' = Me) [2] in this diastereomer the more bulky substituents at C-1 and C-6 of the cyclohexadiene ring (ArCO and CR'R'') have a *trans* configuration; the methyl group at the stereocenter C-3' is found in the proximity of the hydrogen atom at C-6 whereas the alkyl substituent at the same carbon atom is directed "outside" the molecule. These results also show that the stereochemistry of the transformation products cannot be changed by variation of the substituents in 4-position of the phenyl rings (Me, Cl, Br, NO<sub>2</sub>) of **1** or by enhancing the steric demand of the alkyl groups at the nitrogen (Me, Et, *i*-Pr) or at C-3 (Et, *n*-Pr, *i*-Pr) of **2/3**.

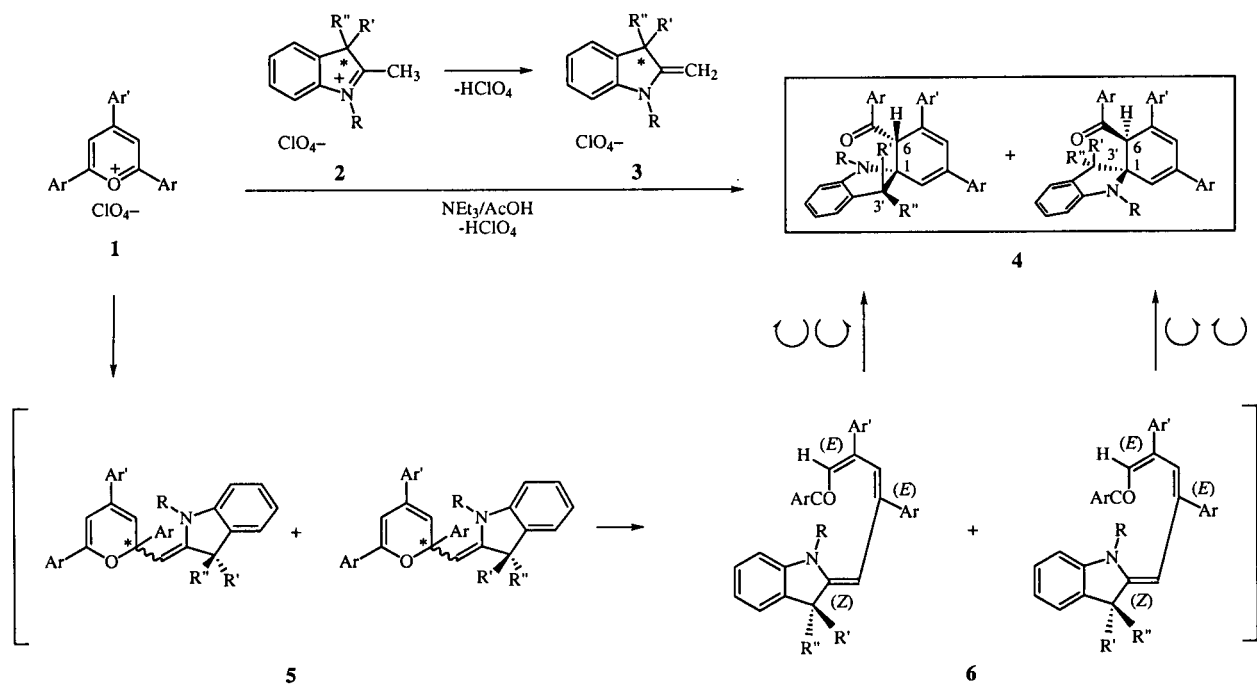
In further experiments the transformation of the pyrilium salt **1a** with the *in situ* generated methyleneindolines **3f-h** possessing a methyl and a benzyl group at the asymmetric carbon atom was studied under the same reaction conditions. The spiro[cyclohexadiene-indolines] **4m-o** formed as a single racemic diastereomer in 73-86% yield have comparable stereochemical characteristics as the compounds **4a-l**, *i.e.* a *trans* configuration of the more bulky substituents at C-1/C-6, the methyl group at C-3' near the hydrogen at C-6 and an "outside" of the molecule directed benzyl group.

Finally, the pyrilium salt **1a** was reacted with the 3-alkyl-3-arylmethyleneindolines **3i-m** formed by *in situ*

deprotonation of the 3*H*-indolium salts **2i-m**. In all cases only one racemic diastereomer **4p-t** was obtained as transformation product in 68-78% yield. Its stereochemistry at C-1 and C-6 was the same as observed for **4a-o**, but the configuration at C-3' is strongly influenced by the kind of the 3-substituents of the methyleneindolines **3** used. Whereas the 3-methyl substituted 3-aryl derivatives **3i-k** led to the spiro[cyclohexadiene-indolines] **4p-r** in which the methyl group is located in the proximity of the C-6 bonded hydrogen, the 3-ethyl and 3-*n*-propyl homologues **3l,m** gave rise to the spiro[cyclohexadiene-indolines] **4s,t** with an "outside" the molecule directed

alkyl group. The restricted space available for a 3'-substituent near the hydrogen at C-6 obviously determines that in each case from the pair of substituents at C-3' (**4p-r**: Me and Ph/4-Me-C<sub>6</sub>H<sub>4</sub>/4-F-C<sub>6</sub>H<sub>4</sub>; **4s,t**: Et/*n*-Pr and Ph) that one with the lower sterical demand becomes located there and causes in this way the inversion of the stereochemistry at this asymmetric carbon atom on going from **4p-r** to **4s,t**.

The formation of the spiro[cyclohexadiene-indolines] of the type **4** can be explained as for their 3',3'-dimethyl substituted analogues reported [2]: In the first step the 3*H*-indolium perchlorates **2** [8] are deprotonated to the



| 1 | 2/3 | Ar                                 | Ar'  | R            | R' | R''                                | 4 |
|---|-----|------------------------------------|--|--------------|----|------------------------------------|---|
| a | a   | Ph                                 | Ph   | Me           | Me | Et                                 | a |
| b | a   | Ph                                 | 4-Me-C <sub>6</sub> H <sub>4</sub>               | Me           | Me | Et                                 | b |
| c | a   | Ph                                 | 4-Cl-C <sub>6</sub> H <sub>4</sub>               | Me           | Me | Et                                 | c |
| d | a   | Ph                                 | 4-Br-C <sub>6</sub> H <sub>4</sub>               | Me           | Me | Et                                 | d |
| e | a   | Ph                                 | 4-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> | Me           | Me | Et                                 | e |
| f | a   | 4-Me-C <sub>6</sub> H <sub>4</sub> | Ph   | Me           | Me | Et                                 | f |
| g | a   | 4-Cl-C <sub>6</sub> H <sub>4</sub> | Ph   | Me           | Me | Et                                 | g |
| h | a   | 4-Br-C <sub>6</sub> H <sub>4</sub> | Ph   | Me           | Me | Et                                 | h |
| a | b   | Ph                                 | Ph   | Et           | Me | Et                                 | i |
| a | c   | Ph                                 | Ph   | <i>i</i> -Pr | Me | Et                                 | j |
| a | d   | Ph                                 | Ph   | Me           | Me | <i>n</i> -Pr                       | k |
| a | e   | Ph                                 | Ph   | Me           | Me | <i>i</i> -Pr                       | l |
| a | f   | Ph                                 | Ph   | Me           | Me | CH <sub>2</sub> Ph                 | m |
| a | g   | Ph                                 | Ph   | Et           | Me | CH <sub>2</sub> Ph                 | n |
| a | h   | Ph                                 | Ph   | <i>i</i> -Pr | Me | CH <sub>2</sub> Ph                 | o |
| a | i   | Ph                                 | Ph   | Me           | Me | Ph                                 | p |
| a | j   | Ph                                 | Ph   | Me           | Me | 4-Me-C <sub>6</sub> H <sub>4</sub> | q |
| a | k   | Ph                                 | Ph   | Me           | Me | 4-F-C <sub>6</sub> H <sub>4</sub>  | r |
| a | l   | Ph                                 | Ph   | Me           | Ph | Et                                 | s |
| a | m   | Ph                                 | Ph   | Me           | Ph | <i>n</i> -Pr                       | t |

Table 1  
Physical and Analytical Data for the 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-indolines] 4

| No. | -spiro[cyclohexa-2,4-diene-1,2'-indoline]                                | Yield (%) | Mp (°C) | Molecular Formula (Molecular Weight)                                     | C              | Analysis (%) |              |
|-----|--|-----------|---------|--|----------------|--------------|--------------|
|     |  |           |         |  |                | Calcd./Found | H            |
| 4a  | 6-Benzoyl-3'-ethyl-1',3'-dimethyl-3,5-diphenyl-                          | 86        | 162-163 | C <sub>36</sub> H <sub>33</sub> NO<br>(495.7)                            | 87.24<br>87.30 | 6.71<br>6.80 | 2.83<br>2.90 |
| 4b  | 6-Benzoyl-3'-ethyl-1',3'-dimethyl-5-(4-methylphenyl)-3-phenyl-           | 74        | 146-148 | C <sub>37</sub> H <sub>35</sub> NO<br>(509.7)                            | 87.19<br>87.21 | 6.92<br>6.83 | 2.75<br>2.71 |
| 4c  | 6-Benzoyl-5-(4-chlorophenyl)-3'-ethyl-1',3'-dimethyl-3-phenyl-           | 89        | 172-174 | C <sub>36</sub> H <sub>32</sub> ClNO<br>(530.1)                          | 81.57<br>81.60 | 6.08<br>5.99 | 2.64<br>2.64 |
| 4d  | 6-Benzoyl-5-(4-bromophenyl)-3'-ethyl-1',3'-dimethyl-3-phenyl-            | 87        | 180-182 | C <sub>36</sub> H <sub>32</sub> BrNO<br>(574.6)                          | 75.26<br>75.30 | 5.61<br>5.60 | 2.44<br>2.41 |
| 4e  | 6-Benzoyl-3'-ethyl-1',3'-dimethyl-5-(4-nitrophenyl)-3-phenyl-            | 89        | 215-216 | C <sub>36</sub> H <sub>32</sub> N <sub>2</sub> O <sub>3</sub><br>(540.7) | 79.98<br>79.91 | 5.97<br>6.03 | 5.18<br>5.27 |
| 4f  | 3'-Ethyl-1',3'-dimethyl-6-(4-methylbenzoyl)-3-(4-methylphenyl)-5-phenyl- | 90        | 199-200 | C <sub>38</sub> H <sub>37</sub> NO<br>(523.7)                            | 87.15<br>87.20 | 7.12<br>7.20 | 2.67<br>2.72 |
| 4g  | 6-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-3'-ethyl-1',3'-dimethyl-5-phenyl- | 88        | 199-201 | C <sub>36</sub> H <sub>31</sub> Cl <sub>2</sub> NO<br>(564.6)            | 76.59<br>76.60 | 5.53<br>5.60 | 2.48<br>2.55 |
| 4h  | 6-(4-Bromobenzoyl)-3-(4-bromophenyl)-3'-ethyl-1',3'-dimethyl-5-phenyl-   | 90        | 204-206 | C <sub>36</sub> H <sub>31</sub> Br <sub>2</sub> NO<br>(653.5)            | 66.17<br>66.26 | 4.78<br>4.83 | 2.14<br>2.20 |
| 4i  | 6-Benzoyl-1',3'-diethyl-3'-methyl-3,5-diphenyl-                          | 77        | 170-171 | C <sub>37</sub> H <sub>35</sub> NO<br>(509.7)                            | 87.19<br>87.26 | 6.92<br>6.84 | 2.75<br>2.71 |
| 4j  | 6-Benzoyl-3'-ethyl-1'-isopropyl-3'-methyl-3,5-diphenyl-                  | 69        | 185-186 | C <sub>38</sub> H <sub>37</sub> NO<br>(523.7)                            | 87.15<br>87.20 | 7.12<br>7.28 | 2.67<br>2.60 |
| 4k  | 6-Benzoyl-1',3'-dimethyl-3,5-diphenyl-3'- <i>n</i> -propyl-              | 73        | 134-135 | C <sub>37</sub> H <sub>35</sub> NO<br>(509.7)                            | 87.19<br>87.26 | 6.92<br>7.00 | 2.75<br>2.68 |
| 4l  | 6-Benzoyl-3'-isopropyl-1',3'-dimethyl-3,5-diphenyl-                      | 63        | 173-175 | C <sub>37</sub> H <sub>35</sub> NO<br>(509.7)                            | 87.19<br>87.30 | 6.92<br>6.82 | 2.75<br>2.71 |
| 4m  | 6-Benzoyl-3'-benzyl-1',3'-dimethyl-3,5-diphenyl-                         | 75        | 195-196 | C <sub>41</sub> H <sub>35</sub> NO<br>(557.7)                            | 88.29<br>88.36 | 6.33<br>6.40 | 2.51<br>2.59 |
| 4n  | 6-Benzoyl-3'-benzyl-1'-ethyl-3'-methyl-3,5-diphenyl-                     | 86        | 175-176 | C <sub>42</sub> H <sub>37</sub> NO<br>(571.8)                            | 88.23<br>88.18 | 6.52<br>6.45 | 2.45<br>2.49 |
| 4o  | 6-Benzoyl-3'-benzyl-1'-isopropyl-3'-methyl-3,5-diphenyl-                 | 73        | 199-200 | C <sub>43</sub> H <sub>39</sub> NO<br>(585.8)                            | 88.17<br>88.26 | 6.71<br>6.79 | 2.39<br>2.46 |
| 4p  | 6-Benzoyl-1',3'-dimethyl-3',3,5-triphenyl-                               | 72        | 220-222 | C <sub>40</sub> H <sub>33</sub> NO<br>(543.7)                            | 88.36<br>88.42 | 6.12<br>6.20 | 2.58<br>2.63 |
| 4q  | 6-Benzoyl-1',3'-dimethyl-3-(4-methylphenyl)-3,5-diphenyl-                | 68        | 176-177 | C <sub>41</sub> H <sub>35</sub> NO<br>(557.7)                            | 88.29<br>88.18 | 6.33<br>6.44 | 2.51<br>2.60 |
| 4r  | 6-Benzoyl-3-(4-fluorophenyl)-1',3'-dimethyl-3,5-diphenyl-                | 71        | 193-194 | C <sub>40</sub> H <sub>32</sub> FNO<br>(561.7)                           | 85.53<br>85.60 | 5.74<br>5.80 | 2.49<br>2.39 |
| 4s  | 6-Benzoyl-3'-ethyl-1'-methyl-3',3,5-triphenyl-                           | 76        | 209-210 | C <sub>41</sub> H <sub>35</sub> NO<br>(557.7)                            | 88.29<br>88.31 | 6.33<br>6.40 | 2.51<br>2.56 |
| 4t  | 6-Benzoyl-1'-methyl-3',3,5-triphenyl-3- <i>n</i> -propyl-                | 78        | 208-209 | C <sub>42</sub> H <sub>37</sub> NO<br>(571.8)                            | 88.23<br>88.30 | 6.52<br>6.63 | 2.45<br>2.40 |

Table 2  
Spectral Data for the 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-indolines] 4

| Compound   | IR (KBr)                  | UV (CH <sub>3</sub> CN)                  | <sup>1</sup> H-NMR (deuteriochloroform) [a]   |
|------------|---------------------------|--|---|
|            | (cm <sup>-1</sup> )<br>CO | λ <sub>max</sub> (nm)<br>(log ε)         |   |
| 4a [b],[c] | 1679                      | 254 (4.61), 312 (4.03),<br>413 sh (3.13) | 0.58 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.31 (s, 3H, 3'-CH <sub>3</sub> ), 1.52 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 2.43 (s, 3H, 1'-CH <sub>3</sub> ), 5.22 (s, 1H, 6-H), 5.55 (d, 1H, 7'-H), 5.98 (s, 1H, 2-H), 6.82 (s, 1H, 4-H), 6.55-7.61 (m, 18H, arom-H)   |
| 4b         | 1679                      | 254 (4.60), 311 (4.08),<br>417 sh (3.20) | 0.59 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.31 (s, 3H, 3'-CH <sub>3</sub> ), 1.52 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 2.12 (s, 3H, 5-C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ), 2.44 (s, 3H, 1'-CH <sub>3</sub> ), 5.22 (s, 1H, 6-H), 5.57 (d, 1H, 7'-H), 5.96 (s, 1H, 2-H), 6.79 (s, 1H, 4-H), 6.56-7.61 (m, 17H, arom-H) |
| 4c         | 1677                      | 256 (4.62), 312 (4.10),<br>420 sh (3.20) | 0.59 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.29 (s, 3H, 3'-CH <sub>3</sub> ), 1.52 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 2.44 (s, 3H, 1'-CH <sub>3</sub> ), 5.17 (s, 1H, 6-H), 5.57 (d, 1H, 7'-H), 5.99 (s, 1H, 2-H), 6.80 (s, 1H, 4-H), 6.57-7.60 (m, 17H, arom-H)   |
| 4d         | 1679                      | 257 (4.63), 314 (4.12),<br>420 sh (3.20) | 0.59 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.28 (s, 3H, 3'-CH <sub>3</sub> ), 1.52 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 2.44 (s, 3H, 1'-CH <sub>3</sub> ), 5.16 (s, 1H, 6-H), 5.57 (d, 1H, 7'-H), 6.00 (s, 1H, 2-H), 6.81 (s, 1H, 4-H), 6.57-7.59 (m, 17H, arom-H)   |

Table 2 (continued)

| Compound          | IR (KBr)<br>(cm <sup>-1</sup> )<br>CO | UV (CH <sub>3</sub> CN)<br>λ <sub>max</sub> (nm)<br>(log ε) | <sup>1</sup> H-NMR (deuteriochloroform) [a]<br>δ (ppm)  |
|-------------------|---------------------------------------|---|---|
| <b>4e</b>         | 1676                                  | 251 (4.55), 296 sh (4.10),<br>373 (4.04), 446 sh (3.39)     | 0.59 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.27 (s, 3H, 3'-CH <sub>3</sub> ), 1.54 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ),<br>2.45 (s, 3H, 1'-CH <sub>3</sub> ), 5.21 (s, 1H, 6-H), 5.60 (d, 1H, 7'-H), 6.10 (s, 1H, 2-H),<br>6.99 (s, 1H, 4-H), 6.59-7.97 (m, 17H, arom-H)   |
| <b>4f</b>         | 1677                                  | 262 (4.71), 313 (4.04),<br>403 sh (3.19)                    | 0.58 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.29 (s, 3H, 3'-CH <sub>3</sub> ), 1.52 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 2.27 (s, 3H,<br>3-C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ), 2.32 (s, 3H, 6-COC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ), 2.44 (s, 3H, 1'-CH <sub>3</sub> ), 5.16 (s, 1H, 6-H),<br>5.61 (d, 1H, 7'-H), 5.93 (s, 1H, 2-H), 6.80 (s, 1H, 4-H), 6.55-7.50 (m, 16H, arom-H)   |
| <b>4g</b>         | 1680                                  | 260 (4.72), 313 (4.05),<br>420 sh (3.11)                    | 0.58 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.29 (s, 3H, 3'-CH <sub>3</sub> ), 1.50 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ),<br>2.44 (s, 3H, 1'-CH <sub>3</sub> ), 5.15 (s, 1H, 6-H), 5.63 (d, 1H, 7'-H), 5.95 (s, 1H, 2-H),<br>6.74 (s, 1H, 4-H), 6.58-7.51 (m, 16H, arom-H)   |
| <b>4h</b>         | 1679                                  | 263 (4.74), 313 sh (4.05),<br>420 sh (3.06)                 | 0.58 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.29 (s, 3H, 3'-CH <sub>3</sub> ), 1.50 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ),<br>2.44 (s, 3H, 1'-CH <sub>3</sub> ), 5.14 (s, 1H, 6-H), 5.63 (d, 1H, 7'-H), 5.96 (s, 1H, 2-H),<br>6.73 (s, 1H, 4-H), 6.57-7.50 (m, 16H, arom-H)   |
| <b>4i</b>         | 1679                                  | 254 (4.62), 319 (4.05),<br>417 sh (3.16)                    | 0.63 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ) 0.87 (t, 3H, 1'-CH <sub>2</sub> CH <sub>3</sub> ), 1.29 (s, 3H, 3'-CH <sub>3</sub> ),<br>1.57 (m, 2H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 2.41 (m, 1H, 1'-CH <sub>2</sub> CH <sub>3</sub> ), 3.03 (m, 1H, 1'-CH <sub>2</sub> CH <sub>3</sub> ),<br>5.21 (s, 1H, 6-H), 5.51 (d, 1H, 7'-H), 5.94 (s, 1H, 2-H), 6.82 (s, 1H, 4-H),<br>6.54-7.61 (m, 18H, arom-H)   |
| <b>4j</b>         | 1680                                  | 253 (4.60), 312 (4.03),<br>413 sh (3.29)                    | 0.62 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 0.78 (d, 3H, 1'-CH(CH <sub>3</sub> ) <sub>2</sub> ), 1.16 (d, 3H, 1'-CH(CH <sub>3</sub> ) <sub>2</sub> ),<br>1.27 (s, 3H, 3'-CH <sub>3</sub> ), 1.42 (m, 1H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.62 (m, 1H, 3'-CH <sub>2</sub> CH <sub>3</sub> ),<br>3.67 (m, 1H, 1'-CH(CH <sub>3</sub> ) <sub>2</sub> ), 5.27 (s, 1H, 6-H), 6.02 (s, 1H, 2-H), 6.25<br>(d, 1H, 7'-H), 6.78 (s, 1H, 4-H), 6.61-7.60 (m, 18H, arom-H) |
| <b>4k</b>         | 1679                                  | 254 (4.61), 310 (4.04),<br>407 sh (3.15)                    | 0.69 (t, 3H, 3'-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.00 (m, 2H, 3'-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.34 (s, 3H, 3'-CH <sub>3</sub> ),<br>1.45 (m, 2H, 3'-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.44 (s, 3H, 1'-CH <sub>3</sub> ), 5.21 (s, 1H, 6-H), 5.56<br>(d, 1H, 7'-H), 5.99 (s, 1H, 2-H), 6.83 (s, 1H, 4-H), 6.55-7.61 (m, 18H, arom-H)  |
| <b>4l</b>         | 1679                                  | 253 (4.60), 313 (4.06),<br>417 sh (3.19)                    | 0.50 (d, 3H, 3'-CH(CH <sub>3</sub> ) <sub>2</sub> ), 0.79 (d, 3H, 3'-CH(CH <sub>3</sub> ) <sub>2</sub> ), 1.36 (s, 3H, 3'-CH <sub>3</sub> ),<br>2.04 (m, 1H, 3'-CH(CH <sub>3</sub> ) <sub>2</sub> ), 2.37 (s, 3H, 1'-CH <sub>3</sub> ), 5.25 (s, 1H, 6-H), 5.50 (d,<br>1H, 7'-H), 6.08 (s, 1H, 2-H), 6.82 (s, 1H, 4-H), 6.55-7.61 (m, 18H, arom-H)  |
| <b>4m</b>         | 1680                                  | 253 (4.63), 312 (4.06),<br>413 sh (3.11)                    | 1.27 (s, 3H, 3'-CH <sub>3</sub> ), 2.51 (s, 3H, 1'-CH <sub>3</sub> ), 2.76 (d, J = 12 Hz, 1H, 3'-CH <sub>2</sub> Ph),<br>2.80 (d, J = 12 Hz, 1H, 3'-CH <sub>2</sub> Ph), 5.25 (s, 1H, 6-H), 5.63 (d, 1H, 7'-H),<br>6.12 (s, 1H, 2-H), 6.88 (s, 1H, 4-H), 6.15-7.66 (m, 23H, arom-H)   |
| <b>4n</b>         | 1678                                  | 254 (4.62), 311 (4.07),<br>420 sh (3.15)                    | 0.98 (t, 3H, 1'-CH <sub>2</sub> CH <sub>3</sub> ), 1.26 (s, 3H, 3'-CH <sub>3</sub> ), 2.48 (m, 1H, 1'-CH <sub>2</sub> CH <sub>3</sub> ),<br>2.75 (d, J = 12 Hz, 1H, 3'-CH <sub>2</sub> Ph), 2.90 (d, J = 12 Hz, 1H, 3'-CH <sub>2</sub> Ph),<br>3.10 (m, 1H, 1'-CH <sub>2</sub> CH <sub>3</sub> ), 5.25 (s, 1H, 6-H), 5.58 (d, 1H, 7'-H), 6.08 (s, 1H,<br>2-H), 6.88 (s, 1H, 4-H), 6.13-7.67 (m, 23H, arom-H)  |
| <b>4o</b>         | 1681                                  | 253 (4.62), 313 (4.10),<br>413 sh (3.42)                    | 0.84 (d, 3H, 1'-CH(CH <sub>3</sub> ) <sub>2</sub> ), 1.26 (s, 3H, 3'-CH <sub>3</sub> ), 1.29 (d, 3H, 1'-CH(CH <sub>3</sub> ) <sub>2</sub> ),<br>2.78 (s, 2H, 3'-CH <sub>2</sub> Ph), 3.76 (m, 1H, 1-CH(CH <sub>3</sub> ) <sub>2</sub> ), 5.31 (s, 1H, 6-H), 6.16<br>(s, 1H, 2-H), 6.31 (d, 1H, 7'-H), 6.83 (s, 1H, 4-H), 6.09-7.66 (m, 23H, arom-H)   |
| <b>4p [b],[c]</b> | 1680                                  | 252 (4.62), 313 (4.08),<br>403 sh (3.20)                    | 1.92 (s, 3H, 3'-CH <sub>3</sub> ), 2.29 (s, 3H, 1'-CH <sub>3</sub> ), 4.92 (s, 1H, 2-H), 5.46 (s, 1H, 6-H),<br>5.73 (d, 1H, 7'-H), 6.86 (s, 1H, 4-H), 6.64-7.72 (m, 18H, arom-H)  |
| <b>4q</b>         | 1680                                  | 252 (4.61), 314 (4.08),<br>403 sh (3.20)                    | 1.90 (s, 3H, 3'-CH <sub>3</sub> ), 2.22 (s, 3H, 3'-C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ), 2.29 (s, 3H, 1'-CH <sub>3</sub> ), 4.95 (s, 1H, 2-H),<br>5.45 (s, 1H, 6-H), 5.71 (d, 1H, 7'-H), 6.75 (s, 1H, 4-H), 6.62-7.71 (m, 22H, arom-H)   |
| <b>4r</b>         | 1681                                  | 253 (4.61), 312 (4.08),<br>400 sh (3.23)                    | 1.90 (s, 3H, 3'-CH <sub>3</sub> ), 2.30 (s, 3H, 1'-CH <sub>3</sub> ), 4.93 (s, 1H, 2-H), 5.44 (s, 1H,<br>6-H), 5.75 (d, 1H, 7'-H), 6.80 (s, 1H, 4-H), 6.65-7.72 (m, 22H, arom-H)  |
| <b>4s [b],[c]</b> | 1679                                  | 252 (4.61), 313 (4.01),<br>397 sh (3.26)                    | 0.51 (t, 3H, 3'-CH <sub>2</sub> CH <sub>3</sub> ), 1.62 (m, 1H, 3-CH <sub>2</sub> CH <sub>3</sub> ), 2.47 (m, 1H, 3'-CH <sub>2</sub> CH <sub>3</sub> ),<br>2.51 (s, 3H, 1'-CH <sub>3</sub> ), 5.22 (s, 1H, 6-H), 5.60 (d, 1H, 7'-H), 6.09 (s, 1H, 2-H),<br>6.36 (s, 1H, 4-H), 6.56-7.65 (m, 23H, arom-H)  |
| <b>4t [b],[c]</b> | 1679                                  | 253 (4.59), 311 (3.99),<br>407 sh (3.18)                    | 0.68 (t, 3H, 3'-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.89 (m, 2H, 3'-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 1.62 (m, 1H,<br>3'-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.32 (m, 1H, 3'-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 2.52 (s, 3H, 1'-CH <sub>3</sub> ), 5.20<br>(s, 1H, 6-H), 5.59 (d, 1H, 7'-H), 6.11 (s, 1H, 2-H), 6.37 (s, 1H, 4-H), 6.55-<br>7.65 (m, 23H, arom-H)  |

[a] 2-H, 4-H, 6-H and 7'-H denote the protons in 2-, 4-, 6- and 7'-position, respectively, and arom-H the protons bonded to the benzene rings. [b] <sup>13</sup>C nmr (deuteriochloroform) **4a** 7.1 (3'-CH<sub>2</sub>CH<sub>3</sub>), 15.4 (3'-CH<sub>3</sub>), 26.9 (3'-CH<sub>2</sub>CH<sub>3</sub>), 29.3 (1'-CH<sub>3</sub>), 44.8 (C-6), 55.9 (C-3'), 77.0 (C-1), 103.9, 114.2, 120.6, 122.3, 122.6, 123.3, 124.2, 125.9, 126.1, 126.5, 126.8, 131.0, 134.4, 137.0, 137.1, 137.9, 138.5, 147.2 (olefinic and aromatic carbons), 195.5 (6-COPh), **4p** 19.0 (3'-CH<sub>3</sub>), 30.0 (1'-CH<sub>3</sub>), 45.6 (C-6), 58.3 (C-3'), 77.5 (C-1), 104.4, 115.8, 122.2, 122.3, 123.2, 123.3, 124.2, 124.4, 125.7, 125.8, 126.0, 126.5, 126.6, 126.9, 131.0, 132.7, 134.8, 136.3, 136.8, 137.1, 138.3, 141.9, 148.8 (olefinic and aromatic carbons), 194.9 (6-COPh), **4s** 7.0 (3'-CH<sub>2</sub>CH<sub>3</sub>), 25.7 (3'-CH<sub>2</sub>CH<sub>3</sub>), 29.5 (1'-CH<sub>3</sub>), 46.4 (C-6), 64.9 (C-3'), 76.9 (C-1), 104.5, 113.5, 119.8, 122.0, 123.0, 124.1, 125.1, 125.2, 125.5, 125.9, 126.1, 126.3, 126.4, 126.7, 127.2, 127.3, 128.8, 130.6, 134.3, 136.4, 136.5, 136.6, 138.7, 138.8, 148.1 (olefinic and aromatic carbons), 195.3 (6-COPh), **4t** 12.7 (3'-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 15.6 (3'-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 29.5 (1'-CH<sub>3</sub>), 35.6 (3'-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 46.4 (C-6), 64.5 (C-3'), 76.8 (C-1), 104.5, 113.6, 119.7, 122.0, 123.0, 124.2, 125.1, 125.2, 125.4, 125.5, 125.7, 125.9, 126.1, 126.3, 126.4, 126.6, 126.7, 126.9, 127.0, 129.2, 130.6, 134.3, 136.5, 136.6, 137.2, 138.7, 148.1 (olefinic and aromatic carbons), 195.3 (6-COPh). [c] Mass spectra: (70 eV), m/z (%) **4a** 495 (54) [M<sup>+</sup>], 390 (100) [M<sup>+</sup>-PhCO], 217 (63), 189 (46), 160 (89), 105 (83) [PhCO<sup>+</sup>], 77 (60) [Ph<sup>+</sup>], **4p** 543 (87) [M<sup>+</sup>], 438 (100) [M<sup>+</sup>-PhCO], 306 (32), 105 (56) [PhCO<sup>+</sup>], 77 (32) [Ph<sup>+</sup>], **4s** 557 (9) [M<sup>+</sup>], 452 (11) [M<sup>+</sup>-PhCO], 306 (63), 222 (100), 105 (23) [PhCO<sup>+</sup>], 77 (18) [Ph<sup>+</sup>], **4t** 571 (87) [M<sup>+</sup>], 466 (100) [M<sup>+</sup>-PhCO], 346 (26), 222 (27), 105 (16) [PhCO<sup>+</sup>], 77 (12) [Ph<sup>+</sup>].

corresponding methyleneindolines **3** which are added as carbon nucleophiles of the enamine type to the preferred position 2 of the pyrylium salts **1** [4] to give the 2*H*-pyran intermediates **5** [9]. As unstable compounds they are easy ring opened to their valence isomers **6**. In the final step a recyclization to the spiro[cyclohexadiene-indolines] **4** takes place. Is this ring closure an electrocyclic reaction its stereochemistry can be predicted by the Woodward-Hoffmann rules [10]. Since  $6\pi$ -electrons are involved the thermal recyclization should be a disrotatory process in which the enantiomers of the racemic spiro[cyclohexadiene-indolines] **4** are formed from the enantiomers of (*E*),(*E*),(*Z*)-configured merocyanines **6** in consideration of the two possible rotation directions of the  $\pi$ -orbitals creating the C-1/C-6 single bond in **4**. The configuration of the double bond of the ArCOCH=CAR' moiety in **6** is determined by the electrocyclic ring opening of the 2*H*-pyran intermediates **5** known to proceed *via* (*E*)-selectivity [9]. Applying the classification principle of pyrylium ring transformations [11] the reaction  $1 + 3 \rightarrow 4$  is of the 2,5-[ $C_4 + C_2$ ] type since the cyclohexadiene ring of **4** is built up from four carbon atoms of the pyrylium cation and two C-atoms of the methyleneindoline connecting the positions 2 and 5 of **1** by a  $C_2$ -chain.

For an unequivocal structure elucidation of the spiro[cyclohexadiene-indolines] **4**, X-ray structure determinations of the compounds **4a**, **4p**, and **4t** as representative examples were performed. Figure 1 shows the ellipsoid drawings of the molecular structures and the atom numbering schemes; selected bond lengths and angles are summarized in Table 3. The results of the structure determinations clearly indicate the configuration of the stereocenters C-1, C-6, and C-3' of the spiro[cyclohexadiene-indolines] **4** as discussed above. Comparing bond lengths and angles determined for the three compounds it becomes evident that the variation of the substituents at C-3' has only a small influence on the molecular framework (*cf.* Table 3).

The results of the elemental analyses and the spectroscopic data (*cf.* Table 1 and 2) are in agreement with the structure of the spiro[cyclohexadieneindolines] **4**. In the  $^1\text{H}$  nmr spectra the nitrogen bonded methyl group of **4a-h**, **4k-m** and **4p-t** causes a singlet at 2.29-2.52 ppm. The methyl substituent at C-3' in **4a-o** is responsible for a further singlet at 1.26-1.36 ppm which is downfield shifted in the 3'-aryl derivatives **4p-r** to 1.90-1.92 ppm. All signals of the other alkyl substituents of **4** show the expected pattern. The singlet of the methine hydrogen at C-6 can be located at 5.14-5.46 ppm. Whereas this signal is only slightly influenced by configurational changes at C-3', the singlets of the 2-H and 4-H protons are very sensitive toward such changes. The first one appears in **4a-o** and **4s,t** at 5.93-6.16 ppm and it is upfield shifted beyond the

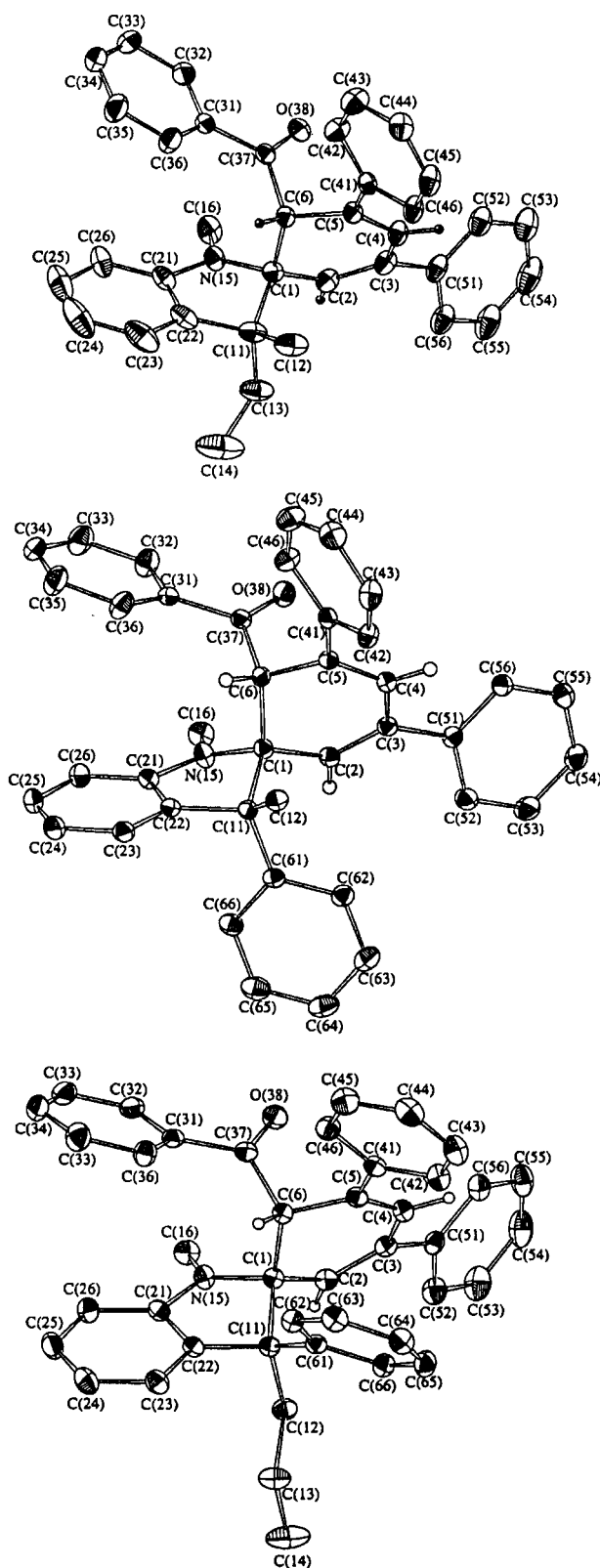


Figure 1. Ellipsoid drawings [12] of the molecular structures of the spiro[cyclohexadiene-indolines] **4a** (top), **4p** (middle) and **4t** (below) together with the atomic numbering schemes (only one enantiomer shown).

Table 3  
Selected Bond Lengths and Bond Angles of the Spiro-  
[cyclohexadiene-indolines] **4a**, **4p** and **4t**

|                           | <b>4a</b> | <b>4p</b> | <b>4t</b> |
|---------------------------|-----------|-----------|-----------|
| Selected bond lengths (Å) |           |           |           |
| C1-C6                     | 1.570(3)  | 1.567(2)  | 1.569(2)  |
| C1-C2                     | 1.505(3)  | 1.504(2)  | 1.503(2)  |
| C2-C3                     | 1.337(3)  | 1.338(2)  | 1.343(2)  |
| C3-C4                     | 1.468(3)  | 1.471(2)  | 1.467(2)  |
| C4-C5                     | 1.331(3)  | 1.335(2)  | 1.339(2)  |
| C5-C6                     | 1.520(3)  | 1.517(2)  | 1.518(2)  |
| C1-C11                    | 1.580(3)  | 1.605(2)  | 1.609(2)  |
| C1-N15                    | 1.484(3)  | 1.477(2)  | 1.484(2)  |
| Selected bond angles (°)  |           |           |           |
| C11-C1-N15                | 100.5(2)  | 100.4(1)  | 101.3(1)  |
| C2-C1-C6                  | 110.6(2)  | 110.5(1)  | 110.8(1)  |
| C1-C2-C3                  | 123.6(2)  | 122.5(1)  | 123.2(1)  |
| C2-C3-C4                  | 119.2(2)  | 119.0(1)  | 119.0(1)  |
| C3-C4-C5                  | 122.7(2)  | 122.4(1)  | 122.3(1)  |
| C4-C5-C6                  | 119.3(2)  | 119.3(1)  | 118.9(1)  |
| C1-C6-C5                  | 113.6(2)  | 111.7(1)  | 112.5(1)  |

methine singlet in **4p-r** to 4.92-4.95 ppm by the anisotropy effect of the adjacent aryl ring. The second one can be found in **4a-r** at 6.73-6.99 ppm in the region where the protons of the benzene rings resonate as a multiplet (6.09-7.97 ppm); it is shifted toward 6.36-6.37 ppm in **4s,t**

because of the same reasons. Finally, the doublet at 5.50-5.75 ppm (**4a-i**, **4k-n**, **4p-t**) can be assigned to the proton at C-7' which resonates at a higher field than the other protons of the benzene rings because of the known shielding effect of the *ortho*-positioned RN-group (R = Me, Et) [13].

To obtain a confirmation of the configuration of the stereocenters at C-1, C-6 and C-3' especially for those compounds, for which no X-ray structure determinations were performed, nOe experiments were carried out. Irradiation into the singlet of the proton at C-6 causes an enhancement of the signal of the methyl group at C-3' of **4a-r** showing the proximity of both groups and hence supporting the assumed molecular structure.

The carbonyl group present in the spiro[cyclohexadiene-indolines] **4** causes in the ir spectra a strong C=O-vibration band at 1676-1681 ppm. A characteristic feature of the uv spectra is an intensive absorption at 251-263 nm usually accompanied by a further band of lower intensity at 310-319 nm with a shoulder reaching up to the visible region.

## EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The <sup>1</sup>H nmr and <sup>13</sup>C nmr spectra were recorded on a Varian Gemini 200 spectrometer (<sup>1</sup>H: 199.975 MHz, <sup>13</sup>C: 50.289

Table 4  
Crystal Data Collection Parameters and Structure Refinement Parameters of the Spiro[cyclohexadiene-indolines] **4a**, **4p** and **4t**

|   | <b>4a</b>   | <b>4p</b>   | <b>4t</b>   |
|---|---|---|---|
| Crystal dimensions (mm <sup>3</sup> )             | 0.55 x 0.50 x 0.15  | 0.35 x 0.30 x 0.30  | 0.40 x 0.20 x 0.10  |
| Measuring temperature (K)                         | 293   | 213   | 213   |
| Formula   | C <sub>36</sub> H <sub>33</sub> NO  | C <sub>40</sub> H <sub>33</sub> NO  | C <sub>42</sub> H <sub>37</sub> NO  |
| M   | 495.63  | 543.67  | 571.73  |
| Crystal system/Space group                        | Monoclinic/C2/c   | Monoclinic/P2 <sub>1</sub> /n   | Monoclinic/P2 <sub>1</sub> /n   |
| Unit cell dimensions                              |   |   |   |
| a (Å)   | 29.350(1)   | 13.399(5)   | 10.271(1)   |
| b (Å)   | 10.141(1)   | 13.915(4)   | 10.911(2)   |
| c (Å)   | 39.700(1)   | 15.755(2)   | 16.300(2)   |
| β (°)   | 109.05(3)   | 90.09(2)  | 102.92(1)   |
| V (Å <sup>3</sup> )                               | 11168(5)  | 2937(1)   | 3086(6)   |
| Z   | 16  | 4   | 4   |
| D <sub>c</sub> (g·cm <sup>-3</sup> )              | 1.179   | 1.229   | 1.231   |
| F(000)  | 4224  | 1152  | 1216  |
| Data collection method                            | Omega scans   | Omega scans   | Omega scans   |
| Linear absorption coefficient (mm <sup>-1</sup> ) | 0.535   | 0.558   | 0.554   |
| Weighting scheme                                  | 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(0.0839P) <sup>2</sup> +7.4961P] with P = (F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3 | 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(0.0558P) <sup>2</sup> +0.7883P] with P = (F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3 | 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(0.0495P) <sup>2</sup> +0.9399P] with P = (F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3 |
| Reflections measured                              | 10094   | 6034  | 6046  |
| θ Range (°)                                       | 5.44-64.99  | 5.37-65.01  | 5.22-65.01  |
| Independent reflections/R <sub>int</sub>          | 9483/0.0222   | 4920/0.0204   | 5086/0.0181   |
| R <sub>1</sub> (obs.)/R <sub>1</sub> (all refl.)  | 0.0526/0.0714   | 0.0358/0.0447   | 0.0392/0.0447   |
| wR2(obs.)/wR2(all refl.)                          | 0.1452/0.1580   | 0.0951/0.1011   | 0.0979/0.1016   |
| Goof (F <sup>2</sup> )                            | 1.035   | 1.006   | 1.071   |
| Programs used                                     | SHELXS-97 [22]<br>SHELXL-97 [23]  | SHELXS-97 [22]<br>SHELXL-97 [23]  | SHELXS-97 [22]<br>SHELXL-97 [23]  |

MHz) and on a Varian Gemini 2000 spectrometer ( $^1\text{H}$ : 200.041 MHz,  $^{13}\text{C}$ : 50.305 MHz) in deuterochloroform 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 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** [14], **1b** [15], **1c,e** [16], **1d** [17] and **1f-h** [18] were synthesized according to literature procedures. The preparation of the 3*H*-indolium perchlorates **2a-c**, **2f-i**, **2l,m** and of 1,3,3-trimethyl-2-*n*-propyl-, 2-isopropyl-1,3,3-trimethyl-, 1,3,3-trimethyl-2-(4-methylphenyl)- as well as 2-(4-fluorophenyl)-1,3,3-trimethyl-3*H*-indolium perchlorate has been reported in a previous paper [6].

Synthesis of the 3*H*-Indolium Perchlorates **2d,e** and **2j,k** by Plancher Rearrangement [19]. General Procedure [20, 21].

To 8 mmoles of the corresponding 2-substituted 1,3,3-trimethyl-3*H*-indolium perchlorate, 3 ml of 1-butanol and 9 ml of 1,5-pentanediol were added. The reaction mixture was refluxed for two hours. After cooling to about 80° 10 ml of absolute ethanol were added. The crystalline products obtained by further cooling were filtered with suction, washed with ethanol and ether and purified by dissolving in a minimal amount of hot acetonitrile and subsequent precipitation with ether.

#### 1,2,3-Trimethyl-3-*n*-propyl-3*H*-indolium Perchlorate (**2d**).

This compound was obtained according to the general procedure from 1,3,3-trimethyl-2-*n*-propyl-3*H*-indolium perchlorate in 78% yield, mp 153-154°;  $^1\text{H}$  nmr (dimethyl- $d_6$  sulfoxide):  $\delta$  0.66 (t, 3H, 3- $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.66 (m, 2H, 3- $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.47 (s, 3H, 3- $\text{CH}_3$ ), 2.04 (m, 2H, 3- $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.74 (s, 3H, 2- $\text{CH}_3$ ), 3.96 (s, 3H, 1- $\text{CH}_3$ ), 7.56-7.89 (m, 4H, arom-H).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{20}\text{ClNO}_4$ : C, 55.72; H, 6.68; N, 4.64. Found: C, 55.60; H, 6.72; N, 4.60.

#### 3-Isopropyl-1,2,3-trimethyl-3*H*-indolium Perchlorate (**2e**).

This compound was obtained according to the general procedure from 2-isopropyl-1,3,3-trimethyl-3*H*-indolium perchlorate in 90% yield, mp 266-267° dec;  $^1\text{H}$  nmr (dimethyl- $d_6$  sulfoxide):  $\delta$  0.33 (d, 3H, 3- $\text{CH}(\text{CH}_3)_2$ ), 1.15 (d, 3H, 3- $\text{CH}(\text{CH}_3)_2$ ), 1.53 (s, 3H, 3- $\text{CH}_3$ ), 2.43 (m, 1H, 3- $\text{CH}(\text{CH}_3)_2$ ), 2.79 (s, 3H, 2- $\text{CH}_3$ ), 4.02 (s, 3H, 1- $\text{CH}_3$ ), 7.59-7.94 (m, 4H, arom-H).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{20}\text{ClNO}_4$ : C, 55.72; H, 6.68; N, 4.64. Found: C, 55.80; H, 6.70; N, 4.61.

#### 1,2,3-Trimethyl-3-(4-methylphenyl)-3*H*-indolium Perchlorate (**2j**).

This compound was obtained by the general procedure from 1,3,3-trimethyl-2-(4-methylphenyl)-3*H*-indolium perchlorate in 71% yield, mp 228-229°;  $^1\text{H}$  nmr (dimethyl- $d_6$  sulfoxide):  $\delta$  1.87 (s, 3H, 3- $\text{CH}_3$ ), 2.21 (s, 3H, 3- $\text{C}_6\text{H}_4\text{CH}_3$ ), 2.57 (s, 3H, 2- $\text{CH}_3$ ), 4.06 (s, 3H, 1- $\text{CH}_3$ ), 7.06-7.97 (m, 8H, arom-H).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}\text{ClNO}_4$ : C, 61.80; H, 5.76; N, 4.00. Found: C, 61.70; H, 5.81; N, 3.99.

#### 3-(4-Fluorophenyl)-1,2,3-trimethyl-3*H*-indolium Perchlorate (**2k**).

This compound was obtained by the general procedure from 2-(4-fluorophenyl)-1,3,3-trimethyl-3*H*-indolium-perchlorate in 72% yield, mp 214-215°;  $^1\text{H}$  nmr (dimethyl- $d_6$  sulfoxide):  $\delta$

1.90 (s, 3H, 3- $\text{CH}_3$ ), 2.59 (s, 3H, 2- $\text{CH}_3$ ), 4.04 (s, 3H, 1- $\text{CH}_3$ ), 7.14-7.98 (m, 8H, arom-H).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{17}\text{ClFNO}_4$ : C, 57.72; H, 4.84; N, 3.96. Found: C, 57.80; H, 4.90; N, 4.00.

Preparation of 1',3',3'-Trisubstituted 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2'-indolines] **4** from 2,4,6-Triarylpyrylium Perchlorates **1** and 1,3,3-Trisubstituted 2-Methyl-3*H*-indolium Perchlorates **2**. General Procedure (cf. Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate **1**, 5 mmoles 3*H*-indolium perchlorate **2**, 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-indolines] **4** formed crystallized after cooling. They were filtered with suction, washed with ethanol and recrystallized from ethanol/chloroform.

#### X-Ray Structure Determinations.

Appropriate crystals of the spiro[cyclohexadiene-indolines] **4a**, **4p** and **4t** were obtained by slow cooling of an ethanol/chloroform solution.

The X-ray experiments were carried out on a single crystal diffractometer CAD4 (Enraf Nonius) with graphite-monochromated  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). The structures were solved using direct methods and difference Fourier techniques [22] and refined by a full-matrix least squares procedure on  $F^2$  [23]. Anisotropic displacement parameters have been applied for all non hydrogen atoms.

More details on data collections and structure determinations are summarized in Table 4. Further details have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 118807 (**4a**), CCDC 118808 (**4p**) and CCDC 118809 (**4t**), respectively.

#### Acknowledgement.

The financial support by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie is gratefully appreciated. We thank Professor J. Strähle (Tübingen) for the opportunity to measure the X-ray data.

#### REFERENCES AND NOTES

- [1] Part XVII: T. Zimmermann, *J. Heterocyclic Chem.*, **36**, 813 (1999).
- [2] T. Zimmermann and M. Pink, *J. Prakt. Chem./Chem.-Ztg.*, **337**, 368 (1995).
- [3] O. Brede, L. Goebel, and T. Zimmermann, *J. Inf. Rec. Mater.*, **22**, 397 (1996); L. Goebel, O. Brede, and T. Zimmermann, *Radiat. Phys. Chem.*, **47**, 369 (1996); O. Brede, L. Goebel, and T. Zimmermann, *J. Phys. Chem. A*, **101**, 4103 (1997); T. Häupl, T. Zimmermann, R. Herrmann, and O. Brede, *Chem. Phys. Letters*, **291**, 215 (1998).
- [4a] A. T. Balaban, A. Dinculescu, G. N. Dorofeenko, G. W. Fischer, A. V. Koblik, V. V. Mezheritskii, and W. Schroth, Pyrylium Salts. Syntheses, Reactions and Physical Properties, *Advances in Heterocyclic Chemistry*, Suppl. 2, Academic Press, New York, 1982; [b] W. Schroth, W. Dölling, and A. T. Balaban, in Houben-Weyl, Vol E7b, R. P. Kreher, ed, Thieme, Stuttgart, 1992, pp 755-1014.
- [5] Recent review on indoles and their derivatives: H. Döpp, D. Döpp, U. Langer, and B. Gerding, in Houben-Weyl, Vol E6b<sub>1</sub>/E6b<sub>2</sub>, R. P. Kreher, ed, Thieme, Stuttgart, 1994, pp 546-1354.

- [6] For a facile synthesis of 3*H*-indolium perchlorates see: T. Zimmermann, *J. Heterocyclic Chem.*, (submitted).
- [7] The racemic spiro[cyclohexadiene-indolines] **4** (R' = R" = Me) can be separated by enantioselective liquid chromatography into the enantiomers enabling the determination of kinetic parameters for the thermal racemization: T. Zimmermann, N. Pustet, and A. Mannschreck, *Monatshfte Chem.*, **130**, 355 (1999).
- [8] The asterisk in a structural formula indicates an asymmetric carbon atom without specification of the stereochemistry.
- [9] For reviews on 2*H*-pyrans see: J. Kuthan, *Adv. Heterocyclic Chem.*, **34**, 145 (1983); J. Kuthan, P. Sebek, and S. Böhm, *Adv. Heterocyclic Chem.*, **62**, 20 (1995); K. Ohketa and K.-Y. Akiba, *Adv. Heterocyclic Chem.*, **65**, 283 (1996).
- [10] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); R. B. Woodward and R. Hoffmann, *Die Erhaltung der Orbitalsymmetrie*, Verlag Chemie, Weinheim, 1970; N. T. Anh, *Die Woodward-Hoffmann-Regeln und ihre Anwendung*, Verlag Chemie, Weinheim, 1972.
- [11] For the classification of pyrylium ring transformations see ref [2a].
- [12] L. Zsolnai, ZORTEP - A Thermal Ellipsoid Drawing Program, University of Heidelberg, Germany, 1997.
- [13] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, Thieme, Stuttgart, New York, 1997, p 116.
- [14] A. T. Balaban and C. Toma, *Tetrahedron*, Supplement **7**, 1 (1966).
- [15] A. Mistr, M. Vavra, J. Skoupy, and R. Zahradnik, *Collect. Czech. Chem. Commun.*, **37**, 1520 (1972).
- [16] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Liebigs Ann. Chem.*, **661**, 1 (1963).
- [17] G. N. Dorofeenko, S. V. Krivun, and V. V. Mezheritskii, *Zh. Obshch. Khim.*, **35**, 632 (1963).
- [18] G. W. Fischer and M. Herrmann, *J. Prakt. Chem.*, **326**, 287 (1984).
- [19] G. Plancher, *Gazz. Chim. Ital.*, **28** II, 374 (1898), *Chem. Zentralbl.* 282 (1899 I); G. Plancher and A. Bonavia, *Atti R. Acad. Naz. Lincei* [5], **9**, 1 (1900), *Chem. Zentralbl.*, 867 (1900 I), *Gazz. Chim. Ital.*, **32** II, 398 (1900), *Chem. Zentralbl.*, 863 (1903 I).
- [20] C. Reichardt, H.-D. Engel, R. Allmann, D. Kucharczyk, and M. Krestel, *Chem. Ber.*, **123**, 565 (1990).
- [21] A. Schinabeck, PhD Thesis, University of Regensburg, Germany, 1998.
- [22] G. Sheldrick, SHELXS-97, A Program for the Solution of X-Ray Crystal Structures, University of Göttingen, Germany, 1997.
- [23] G. Sheldrick, SHELXS-97, A Program for the Refinement of X-Ray Crystal Structures, University of Göttingen, Germany, 1997.