

Ring Transformations of Heterocyclic Compounds. XVI [1].
Spiro[cyclohexadiene-dihydroacridines]. A Novel Class of
Spirodihydroacridines by Ring Transformation of Pyrylium Salts
with 9-Methylacridine and its Quaternary Salts

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Dedicated to Dr. habil. G. W. Fischer on the occasion of his 60th birthday

2,4,6-Triarylpyrylium salts **1** react with the *in situ* generated anhydrobase of 9,10-dimethylacridinium methosulfate (**2a**) in the presence of anhydrous sodium acetate in ethanol by a 2,5-[C₄+C₂] pyrylium ring transformation to give the hitherto unknown 6-aryl-3,5-diaryl-10'-methylspiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridines] **3**. When the pyrylium perchlorate **1a** is treated under the same conditions with the *N*-ethyl, *N*-allyl or *N*-benzyl substituted acridinium salts **2b-d** a dealkylation of these salts occurs and the *N*-unsubstituted spiro[cyclohexadiene-dihydroacridine] **4a** is formed. The same compounds **4** can also be obtained by transformation of the pyrylium salts **1** with 9-methylacridine (**7**) and triethylamine/acetic acid in ethanol. Structure elucidation is performed by an X-ray crystal structure determination of the spiro[cyclohexadiene-dihydroacridine] **3a**. Spectroscopic data of the transformation products and their mode of formation are discussed.

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In a previous paper of this series we reported on the diastereoselective synthesis of 6-aryl-3,5-diarylspro[cyclohexa-2,4-diene-1,2'-indolines] by ring transformation of 2,4,6-triarylpyrylium salts **1** [2] with 3,3-dimethyl-2-methyleneindolines (Fischer base and derivatives thereof) [3]. The spiro compounds obtained in this way represent a novel class of photochromic substances [4]: Their irradiation with visible light under stationary conditions (Xenon high pressure lamp) or by laser flash photolysis causes an electrocyclic ring opening to coloured merocyanines which can be recycled with visible light or by heat to the starting spiroindolines [5]. Since photochromic compounds possess valuable properties for a wide range of technical applications, such as reversible data storage or the conversion of sun energy, enormous efforts have been undertaken to find new types of such systems [4]. So we have focused our investigations in the area of pyrylium ring transformations with anhydrobases of cationic nitrogen heterocycles on the question if by a systematic variation of the structure of 3,3-dimethyl-2-methyleneindolines other novel photochromic spiro compounds can be obtained.

One possibility for a variation is the substitution of the carbon atom in position 3 including the two methyl groups bonded on it by an heteroatom or an heteroatom containing group such as NR (R = alkyl), S or O. When the pyrylium perchlorates **1** were treated with *in situ*

generated anhydrobases of 2-methyl-1*H*-benzimidazolium or 2-methylbenzothiazolium salts unfortunately no spiro compounds but the corresponding azolium salts with a 2,4,6-triarylphenyl substituent in position 2 were obtained [6]. In contrast to these reactions the transformation of the pyrylium perchlorates **1** with anhydrobases of 2-methylbenzoxazolium salts gave instead of 2,4,6-triarylphenyl substituted benzoxazolium compounds 2-[*N*-2-hydroxyphenyl]amino]-4,6-diarylbenzophenones [1]. The fact that this transformation could only be explained by assuming the formation of spiro[cyclohexadiene-benzoxazolines] as intermediates [1] encouraged us to continue our search for reactions leading to novel spiro compounds.

Another possibility for a structure variation of the 3,3-dimethyl-2-methyleneindolines consists in the replacement of the five membered nitrogen heterocycle by a six membered one. Hence, the pyrylium perchlorates **1** were treated with *in situ* generated anhydrobases of 2- and 4-methylpyridinium as well as *N,N*-linked 4,4-dimethylbispyridinium salts. These reactions also did not lead to spiro compounds but to pyridinium salts in which the methyl groups are replaced by a 2,4,6-triarylphenyl substituent [7,8]. The same reaction pattern was observed if the transformation was carried out with anhydrobases of 2- and 4-methylquinolinium salts; here the quinolinium compounds with a 2,4,6-triarylphenyl

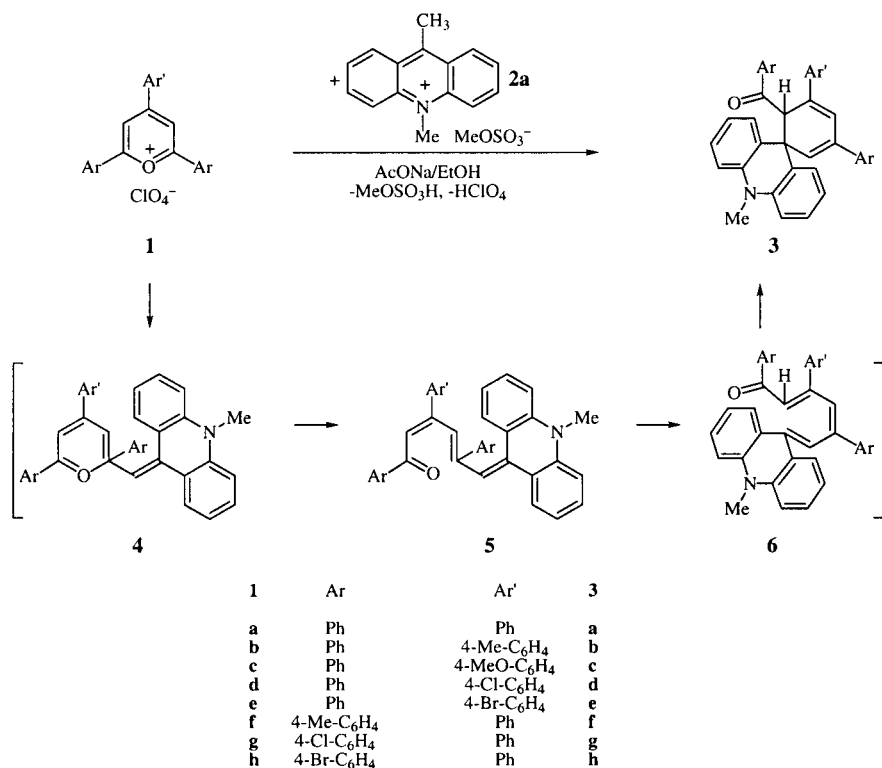
group in the positions 2 and 4, respectively, were obtained [9].

Since quinolinium salts are in principle benzo condensed pyridinium salts one may assume that the linear anellation of two benzene rings to the pyridinium system, i.e. the transformation with anhydrobases of 9-methylacridinium salts [10], would occur according to the same principle. Surprisingly, the reaction proceeds quite differently. In this paper we wish to report on these investigations.

When the 2,4,6-triarylpyrylium perchlorates **1a-h** and the 9,10-dimethylacridinium methosulfate (**2a**) were refluxed in absolute ethanol in the presence of anhydrous sodium acetate instead of 9-(2,4,6-triarylphenyl)-10-methylacridinium perchlorates former unknown 6-aryl-3,5-diaryl-10'-methylspiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridines] **3a-h** were formed in 70-90% yield by pyrylium ring transformation [11] (*cf.* Tables 1 and 2). The reaction products represent a novel type of spirodihydroacridines [10].

the final step to the spiro[cyclohexadiene-dihydroacridines] **3**. Since the cyclohexadiene ring formed contains four carbon atoms of the pyrylium cation and two carbon atoms of the anhydrobase and a connection of the former positions 2 and 5 of the pyrylium ring by a C₂-chain occurs the reaction can be classified as a 2,5-[C₄+C₂] transformation [13].

For an unequivocal structure elucidation of the spiro[cyclohexadiene-dihydroacridines] **3** an X-ray structure determination of the compound **3a** was performed. Figure 1 shows the Schakal plot of the molecular structure of **3a** and the atomic numbering scheme; the crystal data collection parameters and structure refinement parameters, fractional positional parameters as well as selected bond lengths and angles are summarized in the Tables 3-5. An interesting feature of the molecular structure is the stereochemistry of the dihydroacridine system. As already shown for other dihydroacridines with various substitution



One may assume that in the course of the transformation the *in situ* from the 9,10-dimethylacridinium methosulfate (**2a**) generated anhydrobase is added at the preferred position 2 of the pyrylium cation [2] to give the 2*H*-pyran intermediates **4** [12]. Then an electrocyclic ring opening to the acyclic valence isomers **5** takes place from which *via* **6** another electrocyclic process lead in

patterns [18] the relatively sterical overcrowded derivatives of the type **3** also prefer a boat confirmation of the central ring and a "wing-like" arrangement of the two anelated benzene rings.

By trying to extend the ring transformation **1** + **2a** → **3** to acridinium salts bearing other substituents than methyl at the nitrogen atom we made an interesting observation: When

Table 1
Physical and Analytical Data for the 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridines] 3/4

| No. | -spiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridine] | Yield (%) | Mp (°C) | Molecular Formula (Molecular Weight) | Analysis (%) | | |
|-----|---|-----------|---------|---|----------------|--------------|--------------|
| | | | | | C | H | N |
| 3a | 6-Benzoyl-10'-methyl-3,5-diphenyl- | 80 | 197-198 | C ₃₈ H ₂₉ NO (515.7) | 88.51 88.43 | 5.67 5.62 | 2.72 2.71 |
| 3b | 6-Benzoyl-10'-methyl-5-(4-methylphenyl)-3-phenyl- | 70 | 230-231 | C ₃₉ H ₃₁ NO (529.7) | 88.44 88.35 | 5.90 5.85 | 2.64 2.64 |
| 3c | 6-Benzoyl-5-(4-methoxyphenyl)-10'-methyl-3-phenyl- | 80 | 215-216 | C ₃₉ H ₃₁ NO ₂ (545.7) | 85.84 85.76 | 5.73 5.68 | 2.57 2.56 |
| 3d | 6-Benzoyl-5-(4-chlorophenyl)-10'-methyl-3-phenyl- | 84 | 229-230 | C ₃₉ H ₂₈ ClNO (550.1) | 82.97 82.89 | 5.13 5.20 | 2.55 2.44 |
| 3e | 6-Benzoyl-5-(4-bromophenyl)-10'-methyl-3-phenyl- | 90 | 222-224 | C ₃₈ H ₂₈ BrNO (594.6) | 76.77 76.70 | 4.75 4.71 | 2.36 2.35 |
| 3f | 10'-Methyl-6-(4-methylbenzoyl)-3-(4-methylphenyl)-5-phenyl- | 63 | 215-216 | C ₄₀ H ₃₃ NO (543.7) | 88.36 88.28 | 6.12 6.07 | 2.58 2.57 |
| 3g | 6-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-10'-methyl-5-phenyl- | 79 | 224-225 | C ₃₈ H ₂₇ Cl ₂ NO (584.6) | 78.08 78.04 | 4.66 4.50 | 2.40 2.40 |
| 3h | 6-(4-Bromobenzoyl)-3-(4-bromophenyl)-10'-methyl-5-phenyl- | 90 | 226-227 | C ₃₈ H ₂₇ Br ₂ NO (673.5) | 67.77 67.71 | 4.04 4.01 | 2.08 2.08 |
| 4a | 6-Benzoyl-3,5-diphenyl- | 87 | 199-201 | C ₃₇ H ₂₇ NO (501.6) | 88.59 88.50 | 5.43 5.38 | 2.79 2.79 |
| 4b | 6-(4-Methylbenzoyl)-3-(4-methylphenyl)-5-phenyl- | 70 | 213-215 | C ₃₉ H ₃₁ NO (529.7) | 88.44 88.20 | 5.90 5.83 | 2.64 2.68 |
| 4c | 6-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-5-phenyl | 71 | 209-210 | C ₃₇ H ₂₅ Cl ₂ NO (570.5) | 77.90 77.82 | 4.42 4.38 | 2.46 2.45 |
| 4d | 6-(4-Bromobenzoyl)-3-(4-bromophenyl)-5-phenyl | 81 | 219-220 | C ₃₇ H ₂₅ Br ₂ NO (659.4) | 67.39 67.33 | 3.82 3.79 | 2.12 2.12 |

Table 2
Spectral Data for the 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridines] 3/4

| Compound | IR (KBr) | UV (CH ₃ CN) | ¹ H-NMR (dimethyl-d ₆ sulfoxide) [a] |
|-------------|---------------------------------|--|---|
| | (cm ⁻¹) CO, (NH) | λ _{max} (nm) (log ε) | δ (ppm) |
| 3a [b], [c] | 1674 | 242 sh (4.57), 255 (4.61), 284 sh (4.33), 313 sh (4.08) | 3.33 (s, 3H, NCH ₃), 5.14 (s, 1H, 6-H), 6.24 (s, 1H, 2-H), 6.42-7.85 (m, 24H, 4-H + arom-H) |
| 3b | 1676 | 240 sh (4.56), 257 (4.58), 284 sh (4.33), 311 sh (4.11) | 2.08 (s, 3H, CH ₃), 3.34 (s, 3H, NCH ₃), 5.10 (s, 1H, 6-H), 6.19 (s, 1H, 2-H), 6.43-7.82 (m, 23H, 4-H + arom-H) |
| 3c | 1673 | 242 (4.55), 258 (4.54), 313 sh (4.14) | 3.32 (s, 3H, NCH ₃), 3.55 (s, 3H, OCH ₃), 5.12 (s, 1H, 6-H), 6.19 (s, 1H, 2-H), 6.42-7.84 (m, 23H, 4-H + arom-H) |
| 3d | 1676 | 242 sh (4.56), 258 (4.61), 286 sh (4.34), 313 sh (4.13) | 3.35 (s, 3H, NCH ₃), 5.10 (s, 1H, 6-H), 6.25 (s, 1H, 2-H), 6.44-7.85 (m, 23H, 4-H + arom-H) |
| 3e | 1676 | 242 sh (4.54), 259 (4.59), 287 sh (4.30), 313 sh (4.11) | 3.35 (s, 3H, NCH ₃), 5.09 (s, 1H, 6-H), 6.25 (s, 1H, 2-H), 6.48-7.84 (m, 23H, 4-H + arom-H) |
| 3f | 1671 | 243 sh (4.50), 264 (4.64), 314 sh (4.02) | 2.19 (s, 3H, CH ₃), 2.31 (s, 3H, CH ₃), 3.36 (s, 3H, NCH ₃), 5.07 (s, 1H, 6-H), 6.18 (s, 1H, 2-H), 6.48-7.72 (m, 22H, 4-H + arom-H) |
| 3g | 1678 | 244 sh (4.55), 263 (4.70), 314 sh (4.07) | 3.36 (s, 3H, NCH ₃), 5.08 (s, 1H, 6-H), 6.27 (s, 1H, 2-H), 6.51-7.88 (m, 22H, 4-H + arom-H) |
| 3h | 1675 | 243 sh (4.53), 266 (4.74), 314 sh (4.07) | 3.37 (s, 3H, NCH ₃), 5.07 (s, 1H, 6-H), 6.28 (s, 1H, 2-H), 6.52-7.82 (m, 22H, 4-H + arom-H) |
| 4a [b], [c] | 1665, 3342 | 255 (4.60), 311 sh (4.04) | 5.02 (s, 1H, 6-H), 6.26 (s, 1H, 2-H), 6.47-7.82 (m, 24H, 4-H + arom-H), 9.20 (s, 1H, NH) |
| 4b | 1661, 3356 | 264 (4.69), 313 sh (4.06) | 2.18 (s, 3H, CH ₃), 2.31 (s, 3H, CH ₃), 4.95 (s, 1H, 6-H), 6.20 (s, 1H, 2-H), 6.47-7.70 (m, 22H, 4-H + arom H), 9.17 (s, 1H, NH) |
| 4c | 1667, 3356 | 263 (4.75), 311 sh (4.09) | 4.96 (s, 1H, 6-H), 6.29 (s, 1H, 2-H), 6.49-7.86 (m, 22H, 4-H + arom-H), 9.19 (s, 1H, NH) |
| 4d | 1666, 3354 | 266 (4.76), 313 sh (4.06) | 4.95 (s, 1H, 6-H), 6.30 (s, 1H, 2-H), 6.49-7.79 (m, 22H, 4-H + arom-H), 9.19 (s, 1H, NH) |

[a] 2-H, 4-H and 6-H denote the protons in 2-, 4- and 6-position, respectively, and arom H the protons bonded to the benzene rings. [b] ¹³C nmr 3a 31.0 (NCH₃), 45.4 (C-1), 48.4 (C-6), 110.0, 111.5, 118.3, 118.4, 122.0, 122.9, 123.1, 123.3, 123.9, 124.1, 124.9, 125.4, 125.5, 125.6, 125.8, 126.2, 126.5, 126.8, 130.3, 132.3, 134.5, 136.4, 137.2, 137.6, 139.5, 141.0 (carbons of the benzene rings and of the cyclohexadiene system) 194.4 (CO), 4a 45.1 (C-1), 50.1 (C-6), 116.7, 117.7, 117.8, 118.7, 120.2, 122.2, 123.2, 123.8, 124.0, 125.3, 125.5, 125.6, 125.8, 126.5, 126.8, 126.9, 130.0, 131.9, 134.6, 136.1, 137.2, 137.5, 137.6, 139.1 (carbons of the benzene rings and of the cyclohexadiene system), 194.5 (CO). [c] Mass spectra: (70 eV), m/z (%) 3a 515 (14) [M⁺], 410 (100) [M⁺- PhCO], 294 (82), 193 (64), 105 (46) [PhCO⁺], 77 (30) [Ph⁺], 4a 511 (12) [M⁺], 105 (100) [PhCO⁺], 77 (26) [Ph⁺].

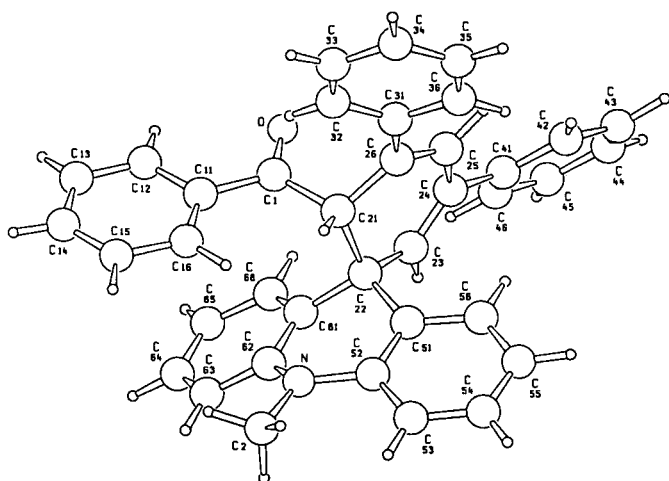


Figure 1. Schakal plot [14] of the molecular structure of the spiro[cyclohexadiene-dihydroacridine] **3a** together with the atomic numbering scheme.

Table 3

Crystal Data Collection and Structure Refinement Parameters

| | |
|---|--|
| Crystal dimensions (mm ³) | 0.40 x 0.30 x 0.15 |
| Formula | C ₃₈ H ₂₉ NO |
| M | 515.62 |
| Crystal system/Space group | Monoclinic/P2 ₁ /c |
| Unit cell dimensions | a = 10.949(1) Å b = 16.308(1) Å c = 16.080(2) Å β = 107.85(1)° |
| V (Å ³) | 2733.0(4) |
| Z | 4 |
| D _c (g cm ⁻³) | 1.253 |
| Radiation (λ) | CuK _α (1.54184 Å) |
| F(000) | 1088 |
| Data collection method | Omega scans |
| Linear absorption coefficient (mm ⁻¹) | 0.573 |
| Weighting scheme | 1/[σ ² (F _o ²)+(0.0457P) ² +0.3036P] with P = (F _o ² +2F _c ²)/3 |
| Reflections measured | 4417 |
| θ range | 5–65° |
| Independent reflections/R _{int} | 2258 |
| R ₁ (obs)/R ₁ (all refl.) | 0.034/0.049 |
| wR2(obs)/wR2(all refl.) | 0.088/0.100 |
| Goof(F ²) | 1.090 |
| Programs used | SDP [15], SHELXS-86 [16], SHELXL-93 [17] |

2,4,6-triphenylpyrylium perchlorate (**1a**) and quaternary acridinium salts with an *N*-ethyl (**2b**), *N*-allyl (**2c**) or *N*-benzyl (**2d**) residue were refluxed in ethanol in the presence of anhydrous sodium acetate not the expected spiro[cyclohexadiene-dihydroacridines] with these substituents at the *N*-atom were obtained but in all cases the dealkylated analogue **4a** was the sole transformation product [19].

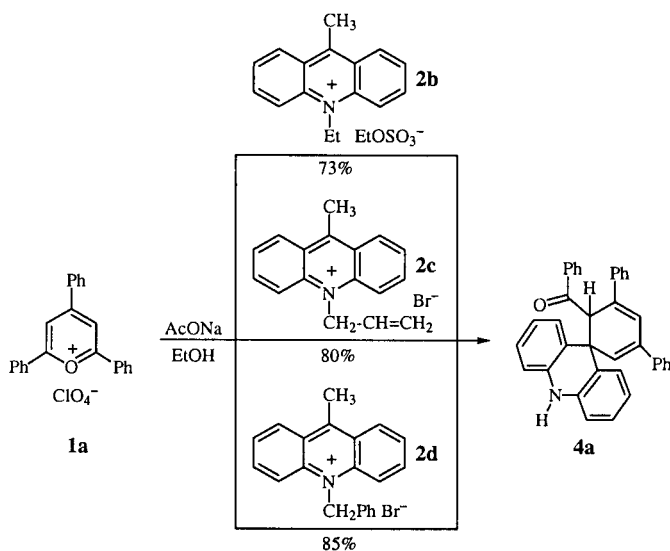
Table 4
Fractional Positional Parameters and Equivalent Thermal Parameter (Å² · 10³) for the Spiro[cyclohexadiene-dihydroacridine] **3a**

| | x | y | z | U(eq) |
|-------|-----------|-----------|------------|--------|
| O | 0.6961(4) | 0.7950(1) | 0.2335(2) | 76(2) |
| N | 0.7730(3) | 0.9412(1) | 0.5377(2) | 57(2) |
| C(1) | 0.6849(4) | 0.8055(2) | 0.3057(2) | 55(2) |
| C(2) | 0.7822(5) | 0.9234(2) | 0.6280(2) | 82(3) |
| C(11) | 0.7299(4) | 0.7403(1) | 0.3746(2) | 63(2) |
| C(12) | 0.7927(3) | 0.6728(2) | 0.3542(3) | 96(3) |
| C(13) | 0.8343(6) | 0.6103(2) | 0.4148(4) | 132(4) |
| C(14) | 0.8192(6) | 0.6157(3) | 0.4940(4) | 132(4) |
| C(15) | 0.7564(4) | 0.6811(2) | 0.5161(3) | 107(3) |
| C(16) | 0.7126(4) | 0.7445(2) | 0.4560(2) | 74(2) |
| C(21) | 0.6245(2) | 0.8845(1) | 0.3267(2) | 46(1) |
| C(22) | 0.7261(3) | 0.9566(1) | 0.3555(2) | 45(1) |
| C(23) | 0.7457(3) | 0.9967(1) | 0.2773(2) | 52(2) |
| C(24) | 0.6560(3) | 1.0008(1) | 0.1989(2) | 49(2) |
| C(25) | 0.5321(3) | 0.9607(2) | 0.1899(2) | 52(1) |
| C(26) | 0.5128(3) | 0.9096(1) | 0.2480(2) | 49(1) |
| C(31) | 0.3858(3) | 0.8727(1) | 0.2392(2) | 48(2) |
| C(32) | 0.3715(3) | 0.7948(2) | 0.2688(2) | 60(2) |
| C(33) | 0.2518(3) | 0.7620(2) | 0.2592(3) | 75(2) |
| C(34) | 0.1434(3) | 0.8059(2) | 0.2201(3) | 79(2) |
| C(35) | 0.1547(3) | 0.8837(2) | 0.1911(3) | 77(2) |
| C(36) | 0.2743(3) | 0.9175(2) | 0.2003(2) | 69(2) |
| C(41) | 0.6727(3) | 1.0521(2) | 0.1281(2) | 50(2) |
| C(42) | 0.5693(4) | 1.0915(2) | 0.0687(2) | 64(2) |
| C(43) | 0.5867(5) | 1.1439(2) | 0.0055(3) | 74(3) |
| C(44) | 0.7056(4) | 1.1588(2) | -0.0005(3) | 79(3) |
| C(45) | 0.8103(5) | 1.1209(2) | 0.0560(3) | 76(3) |
| C(46) | 0.7938(4) | 1.0682(2) | 0.1188(3) | 62(2) |
| C(51) | 0.6743(3) | 1.0193(1) | 0.4066(2) | 47(2) |
| C(52) | 0.6967(3) | 1.0086(2) | 0.4963(2) | 49(2) |
| C(53) | 0.6481(3) | 1.0646(2) | 0.5428(2) | 62(2) |
| C(54) | 0.5785(4) | 1.1309(2) | 0.5010(3) | 70(2) |
| C(55) | 0.5543(4) | 1.1429(2) | 0.4138(3) | 67(2) |
| C(56) | 0.6031(3) | 1.0874(2) | 0.3671(2) | 56(2) |
| C(61) | 0.8522(3) | 0.9209(2) | 0.4151(2) | 47(2) |
| C(62) | 0.8682(3) | 0.9125(2) | 0.5038(2) | 52(2) |
| C(63) | 0.9779(3) | 0.8731(2) | 0.5566(3) | 66(2) |
| C(64) | 1.0675(4) | 0.8431(2) | 0.5215(3) | 71(3) |
| C(65) | 1.0537(4) | 0.8507(2) | 0.4341(3) | 75(2) |
| C(66) | 0.9446(3) | 0.8917(2) | 0.3820(3) | 59(2) |

Table 5

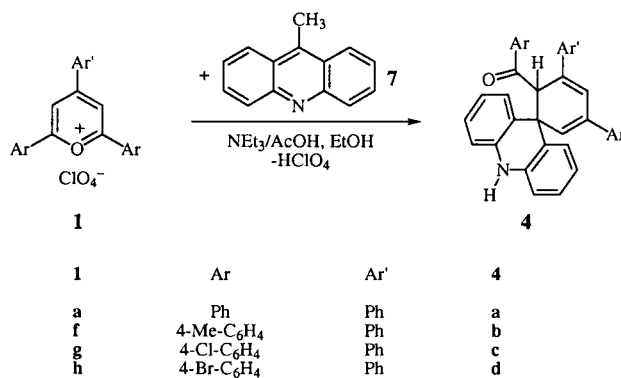
Selected Bond Lengths and Angles in the Spiro[cyclohexadiene-dihydroacridine] **3a**

| Bond Lengths [Å] | | | |
|------------------|----------|-------------|----------|
| C21–C22 | 1.587(3) | C25–C26 | 1.317(5) |
| C22–C23 | 1.491(5) | C21–C26 | 1.521(3) |
| C23–C24 | 1.341(3) | C22–C51 | 1.526(5) |
| C24–C25 | 1.473(5) | C22–C61 | 1.534(3) |
| Bond Angles [°] | | | |
| C51–C22–C61 | 109.3(2) | C24–C25–C26 | 123.7(2) |
| C23–C22–C21 | 110.3(2) | C25–C26–C21 | 119.8(3) |
| C24–C23–C22 | 124.2(3) | C22–C21–C26 | 110.9(2) |
| C23–C24–C25 | 117.2(3) | | |



In a control experiment 10-ethyl-9-methylacridinium ethosulfate (**2b**) and sodium acetate without addition of a pyrylium salt were heated in ethanol. The formation of 9-methylacridine (**7**) (77% isolated yield) showed that under these conditions acridinium salts can be dealkylated [20]. Obviously the two types of products in the ring transformation of the pyrylium perchlorates **1** with the acridine **7** are caused by rate differences of two competing reactions. In the case of the methyl derivative **2a** the deprotonation to the corresponding anhydrobase is faster than the loss of the methyl group and hence *N*-methyl spiro[cyclohexadiene-dihydroacridines] **3** are obtained. The ethyl, allyl or benzyl residue as better cationic leaving groups lead to an inverted order of the rates of the two reactions and so to the formation of *N*-dealkylated spiro[cylohexadiene-dihydroacridines] of the type **4**. Since in these transformations instead of the anhydrobases of **2b-c** *in situ* generated 9-methylacridine (**7**) act as carbon nucleophile it should be possible to react the pyrylium salts **1** with the acridine **7** in a direct manner. Indeed, when the pyrylium perchlorates **1a,f-h** and **7** were refluxed in ethanol in the presence of an equimolar amount of triethylamine and acetic acid the 6-aroyle-3,5-diarylspiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridines] **4a-d** were obtained in 70-81% yield [11] (*cf.* Tables 1 and 2).

The results of the elemental analyses and the spectroscopic data (*cf.* Tables 1 and 2) are in agreement with the structure of the spiro[cyclohexadiene-dihydroacridines] **3/4**. In the ^1H nmr spectra the *N*-methyl group of **3a-h** is responsible for the singulett at 3.32-3.37 ppm; the nitrogen bonded proton of **4a-d** can be located as a singulett at 9.15-9.20 ppm. The aliphatic proton in position 6 and the olefinic proton at C-2 cause the expected singulett (6-H: 4.95-5.19 ppm, 2-H: 6.18-6.35 ppm). Their chemical shifts are comparable to



those ones for the same protons in the structural related spiro[cyclohexadiene-indolines] **A** [3] (6-H: 5.11-5.20 ppm, 2-H: 5.61-6.03 ppm). The singulett expected for the proton at C-4 can not be assigned since it is masked by the multiplett (6.42-7.97 ppm) of the aromatic protons. In the ^{13}C nmr spectra, recorded for the compounds **3a** and **4a**, the presence of the carbonyl group is documented by a signal at 194.4 ppm and 194.5 ppm, respectively. The ir spectra show the carbonyl band (1661-1678 cm^{-1}) in the same region as for the spiro derivatives **A** (1674-1684 cm^{-1}); the sharp band of **4a-d** at 3342-3356 cm^{-1} is the typical one for a secondary amine [21]. Finally, the uv spectra are characterized by a strong absorption around 260 nm.

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ^1H nmr and ^{13}C nmr spectra were recorded on a Varian Gemini 200 spectrometer (199.975 MHz for protons, 50.289 MHz for ^{13}C nuclei, dimethyl- d_6 sulfoxide -25° , hexamethyl disiloxane as internal standard), ir spectra were obtained on a Perkin-Elmer FTIR 2000 spectrophotometer (in potassium bromide) and uv-vis 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** [22], **1b** [23], **1c** [24], **1d** [25], **1e** [26] and **1f-h** [27] were prepared according to literature procedures; 9-methylacridine (**7**) was purchased from Acros.

Synthesis of the Quarternary 9-Methylacridinium Salts **2a-d**.

9,10-Dimethylacridinium Methosulfate **2a**.

This compound was obtained by alkylation of 9-methylacridine (**7**) with dimethyl sulfate as described in reference [28].

10-Ethyl-9-methylacridinium Ethosulfate (**2b**).

9-Methylacridine (**7**) (0.97 g, 5 mmoles) and diethyl sulfate (0.77 g, 5 mmoles) were refluxed in 5 ml of toluene for 30 minutes. After cooling ether was added and the crystals precipitated were filtered by suction, washed with ether and dried to yield 0.37 g (21%) 10-ethyl-9-methylacridinium ethosulfate (**2b**), mp $197-199^\circ$ dec; uv-vis: λ_{max} nm (lg ϵ) 213 (4.21), 252 (5.06), 338 (3.91), 353 (4.22), 385 (3.60), 410 (3.48), 431 (3.27).

Anal. Calcd. for $C_{18}H_{21}NO_4S$: C, 62.23; H, 6.09; N, 4.03. Found: C, 62.00; H, 6.03; N, 4.10.

10-Allyl-9-methylacridinium Bromide (**2c**).

A mixture of 9-methylacridine (**7**) (0.97 g, 5 mmoles), allyl bromide (0.60 g, 5 mmoles) and 10 ml of absolute ethanol was refluxed for 4 hours. After cooling and addition of ether the crystals formed were filtered by suction, washed with ether and dried to give 0.27 g (17%) 10-allyl-9-methylacridinium bromide (**2c**), mp 278-280° dec; uv-vis: λ_{max} nm (lg ϵ) 215 (4.38), 252 (5.07), 345 (3.87), 353 (4.18), 385 (3.59), 412 sh (3.40), 433 (3.11).

Anal. Calcd. for $C_{17}H_{16}BrN$: C, 64.98, H, 5.13, N, 4.46. Found: C, 65.03; H, 5.10; N, 4.52.

10-Benzyl-9-methylacridinium Bromide (**2d**).

This compound was prepared according to the procedure given for the synthesis of **2c** from **7** and benzyl bromide (0.86 g, 5 mmoles), yield 1.03 g (57%), mp 298-300° dec; uv-vis: λ_{max} nm (lg ϵ) 215 (4.47), 252 (5.09), 345 (4.00), 353 (4.30), 386 (3.69), 412 (3.59), 433 (3.33).

Anal. Calcd. for $C_{21}H_{18}BrN$: C, 69.24; H, 4.98; N, 3.84. Found C, 69.20; H, 4.90; N, 3.80.

Preparation of *N*-Methyl Substituted 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridines] **3** from 2,4,6-Triarylpyrylium Perchlorates **1** and 9,10-Dimethylacridinium Methosulfate (**2a**). General Procedure (cf. Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate **1**, 9,10-dimethylacridinium methosulfate (**2a**) (1.60 g, 5 mmoles) and anhydrous sodium acetate (1.23 g, 15 mmoles) were added. The reaction mixture was then refluxed for 2 hours. The spiro[cyclohexadiene-dihydroacridines] **3** formed crystallized in some cases from the hot reaction mixture; otherwise their crystallization was initiated by cooling. They were filtered by suction, washed with water and ethanol and recrystallized from ethanol/xylene.

Reaction of 2,4,6-Triphenylpyrylium Perchlorate (**1a**) with the Acridinium Salts **2b-d** to 6-Benzoyl-3,5-diphenylspiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridine] **4a**.

According to the general procedure for the preparation of the spiro[cyclohexadiene-dihydroacridines] **3** the pyrylium perchlorate **1a** (2.04 g, 5 mmoles) was treated with 5 mmoles of the acridinium salts **2b-d** to give the *N*-unsubstituted spiro compound **4a**, yield 73% (from **2b**), 80% (from **2c**) and 85% (from **2d**), respectively.

Deethylation of 10-Ethyl-9-methylacridinium Ethosulfate (**2b**) with Sodium Acetate in Ethanol.

10-Ethyl-9-methylacridinium ethosulfate (**2b**) (0.28 g, 0.8 mmole), anhydrous sodium acetate (0.20 g, 2.4 mmoles) and 6 ml of ethanol were refluxed for 2 hours. After cooling and addition of a small amount of water the crystals formed were filtered off by suction to give 0.12 g (77%) 9-methylacridine (**7**) which was identical in all respects with an authentic sample.

Preparation of *N*-Unsubstituted 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,9'-9',10'-dihydroacridines] **4** from 2,4,6-Triarylpyrylium Perchlorates **1** and 9-Methylacridine (**7**). General Procedure (cf. Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate **1**, 9-methylacridine (**7**) (0.97 g, 5 mmoles), triethylamine (1.52 g, 15 mmoles) and acetic acid (0.60 g, 10 mmoles) were added and the

resulting reaction mixture was refluxed for 2 hours. The isolation and purification of the spiro[cyclohexadiene-dihydroacridines] **4** was performed according to the general procedure given for the synthesis of the spiro compounds **3**.

X-Ray Structure Determination

Appropriate crystals of the spiro[cyclohexadiene-dihydroacridine] **3a** were obtained by slow cooling of an ethanol/xylene solution.

The X-ray experiment was carried out on a single crystal diffractometer CAD4 (Enraf Nonius) with CuK_{α} radiation at ambient temperature. The lattice parameter were derived by means of 25 high angle reflections. Data collection in the range of Θ between 5 and 65° resulted in 4417 reflections.

Data reduction was done with SPD [15]. The structure was solved applying direct methods with SHELXS-86 [16] and refined with SHELXL-93 [17]. Anisotropic thermal parameters were applied for all non-hydrogen atoms. No unusual thermal ellipsoids were observed. H atom positions were calculated for idealized positions and treated using the 'riding model' option of SHELXL-93 [17]. More details on data collection and structure determination are summarized in Table 3. Table 4 contains the atomic positions and Table 5 selected bond lengths and angles. Further details have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, as Supplementary Publication No. CSD 408462.

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