Ring Transformations of Heterocyclic Compounds. XIX [1]. Spiro[dihydropyridine-indolines] Novel Heterocycles with Two *Spiro*-Condensed *N*-Containing Subunits Easy Accessible by 1,3-Oxazinium Ring Transformation

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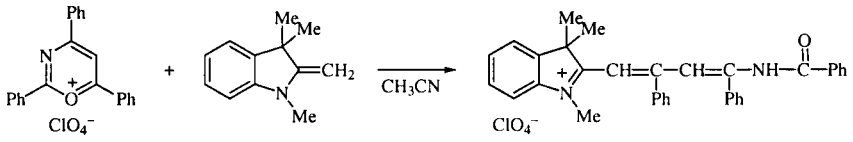
Received September 13, 1999

The synthesis of hitherto unknown 1-benzoyl-1',3',3'-trimethyl-4,6-diphenylspiro[1,2-dihydropyridine-2,2'-indolines] **5** from 2,4,6-triphenyl-1,3-oxazinium tetrafluoroborate (**1b**) and 1,3,3-trimethyl-2-methyleneindolines **2** (used as such or generated *in situ* from the corresponding 3*H*-indolium salts **4**) in the presence of triethylamine in anhydrous acetonitrile by a 3,6-[C_3N+C_2] 1,3-oxazinium ring transformation is reported. Structure elucidation is performed by an X-ray structure determination of the spiro[dihydropyridine-indoline] **5a**. Spectroscopic data of the transformation products and their mode of formation are discussed.

J. Heterocyclic Chem., **37**, 1241 (2000).

1,3-Oxazinium salts ("3-azapyrylium salts") [2], easy accessible from acyclic starting materials, are known to react as compounds possessing a high electron deficient cation with a wide range of nucleophiles i) by ring opening to acyclic products, ii) by addition to substances with an intact 1,3-oxazine moiety or iii) by ring transformation to other heterocycles. Thus, 2,4,6-triphenyl-1,3-oxazinium perchlorate (**1a**) and 1,3,3-trimethyl-2-methyleneindoline (**2a**) (Fischer base), as a typical carbon nucleophile of the enamine type, lead in acetonitrile, without addition of any base, to the indolium dye salt **3** [2,3].

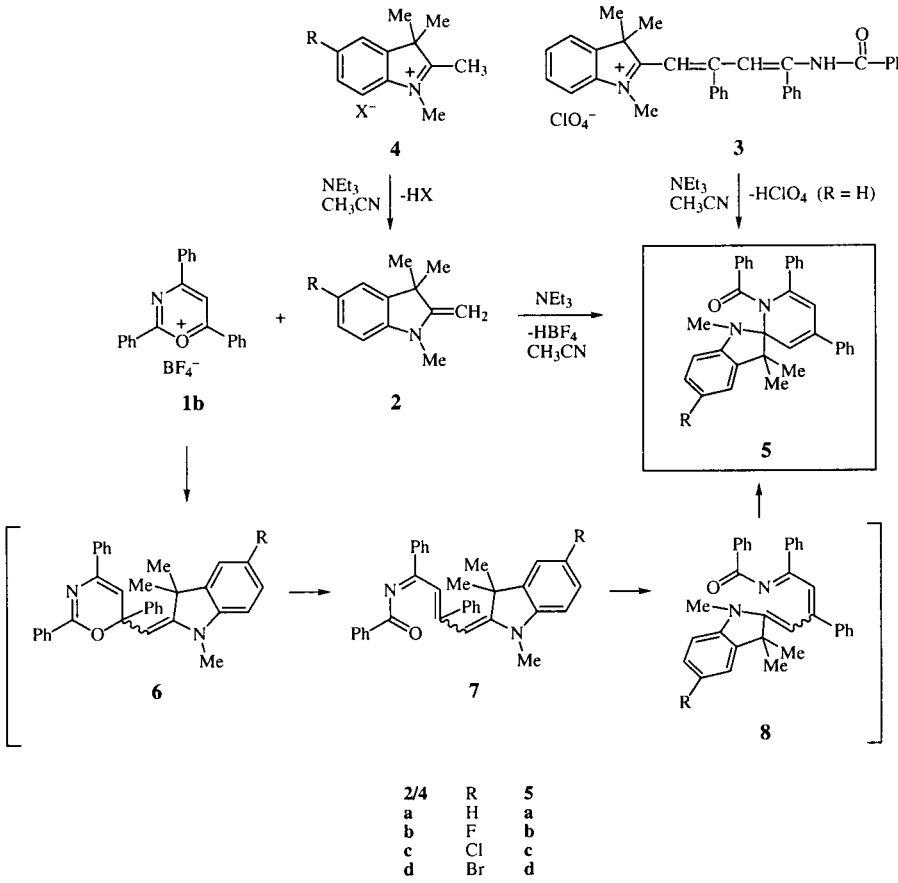


1a **2a** **3**

In previous papers of this series [1,4] it has been shown that the structurally related 2,4,6-triarylpyrylium salts [5] undergo by treatment with the Fischer base and derivatives thereof a ring transformation to spiro[cyclohexadiene-indolines] which represent a novel type of photochromic substances [6]. By variation of the reaction conditions employed for the conversion **1a** + **2a** → **3** it should be possible to influence the course of the reaction with the aim to obtain recyclized products instead of the acyclic indolium derivative **3**. This hypothesis is supported by the observation that the salt **1a** and morpholinocyclohexene as ketone derived enamine can react by ring transformation to give 1-benzoyl-2,4-diphenyl-1,5,6,7-tetrahydroquinoline [2,7]. In the present paper we wish to report on the results of such investigations.

A systematic study was undertaken to determine how the nature of the products obtained from 1,3-oxazinium salts and methyleneindolines depends on the reaction conditions employed. The results clearly indicate that the presence of an appropriate base is a crucial prerequisite to obtain cyclic products. When the 1,3-oxazinium salt **1b** was refluxed in absolute acetonitrile in the presence of triethylamine with the methyleneindolines **2a-d**, used as such or generated *in situ* from the corresponding 3*H*-indolium salts **4** by deprotonation, instead of a ring opening of the 1,3-oxazinium cation the envisaged ring transformation occurs giving rise to the spiro[dihydropyridine-indolines] **5a-d** [8]. As shown by the conversion **3** → **5a** the same type of compounds can also be formed by cyclization of indolium dye salts of type **3** [9] with triethylamine in absolute acetonitrile. Although the yields are only moderate novel heterocycles with two *spiro*-condensed *N*-containing subunits can easily be prepared in this way.

Concerning the mechanism of the ring transformation **1b** + **2** → **5** one may assume that the methyleneindolines **2** are added as carbon nucleophiles of the enamine type such as other *C*-nucleophiles at C-6 of the 1,3-oxazinium cation to give the 6*H*-1,3-oxazine derivatives **6** as the primary intermediates [2]. After electrocyclic ring opening to **7**, followed by isomerization to **8**, in the final step an electro-



cyclic recyclization to the spiro[dihydropyridine-indolines] **5** occurs. As the result of the transformation, a dihydropyridine ring is built from the C_3N-moiety of the 1,3-oxazinium cation and two carbon atoms of the methyleneindoline by connection of the former positions 3 and 6 of **1** with a C_2-chain. Applying the classification principle

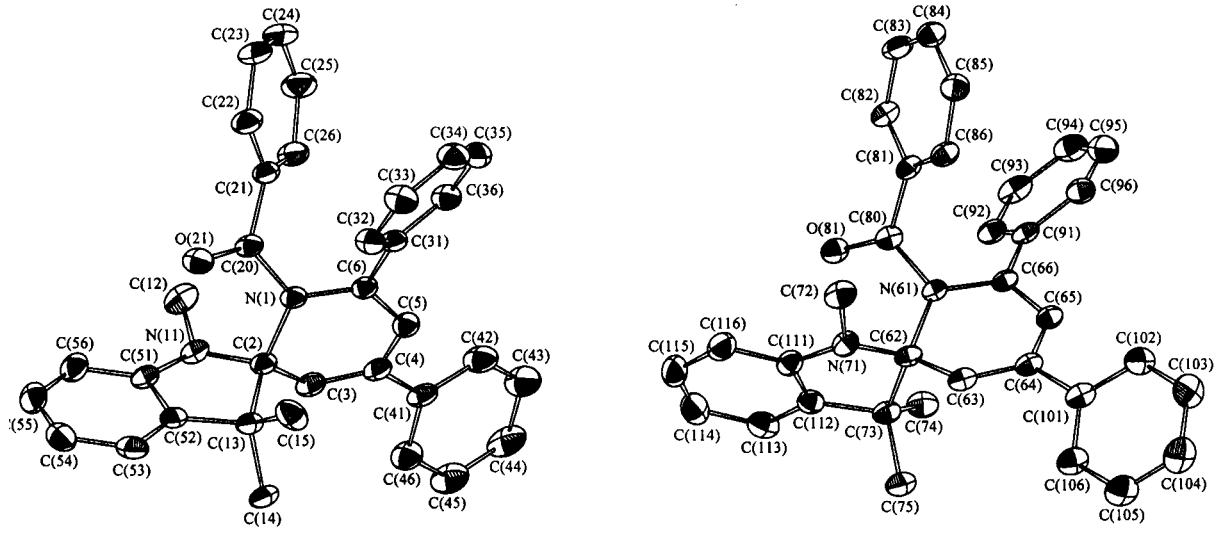


Figure 1. Ellipsoid drawings [11] of the two symmetry-independent molecules of the spiro[dihydropyridine-indoline] **5a** together with the atom numbering schemes.

successfully used for pyrylium ring transformations [10] the reaction can be characterized as a 3,6-[C_3N+C_2] type.

For an unequivocal structure elucidation of the spiro[dihydropyridineindolines] **5** an X-ray structure determination of compound **5a** was performed. The asymmetric unit of the triclinic unit cell contains two independent molecules of **5a** with small differences in bond lengths and angles. Figure 1 shows the ellipsoid drawings of these two molecules and the atom numbering schemes; selected bond lengths and angles are summarized in Table 1.

Table 1

Selected Bond Lengths and Bond Angles of the Two Symmetry-Independent Molecules of the Spiro[dihydropyridine-indoline] **5a**

Selected bond lengths (Å)	
N1-C2/N61-C62	1.513(3)/1.525(3)
C2-C3/C62-C63	1.506(4)/1.507(4)
C3-C4/C63-C64	1.345(4)/1.348(4)
C4-C5/C64-C65	1.450(4)/1.449(4)
C5-C6/C65-C66	1.350(4)/1.331(4)
N1-C6/N61-C66	1.407(4)/1.417(4)
C2-C13/C62-C73	1.586(4)/1.592(4)
C2-N11/C62-N71	1.468(4)/1.447(4)
Selected bond angles (°)	
N11-C2-C13/N71-C62-C73	101.7(2)/102.3(2)
N1-C2-C3/N61-C62-C63	106.2(2)/106.6(2)
C2-C3-C4/C62-C63-C-64	124.3(3)/124.8(3)
C3-C4-C5/C63-C64-C65	118.7(3)/118.1(2)
C4-C5-C6/C64-C65-C66	120.0(3)/121.6(3)
N1-C6-C5/N61-C66-C65	119.8(3)/119.8(2)
C2-N1-C6/C62-N61-C66	120.9(2)/120.6(2)

The results of the elemental analyses and the spectroscopic data are in agreement with the structure of the spiro[dihydropyridine-indolines] **5**. In the ^{1}H nmr spectra the two magnetically non-equivalent methyl groups at C-3' cause the singlets at 1.27-1.29 ppm and 1.74-1.77 ppm; another singlet at 2.78-2.81 ppm can be attributed to the *N*-methyl substituent. The olefinic protons of the 2*H*-dihydropyridine ring at C-3 and C-5 are responsible for two doublets in the range of 5.71-5.81 ppm with a coupling constant of 1.3-1.4 Hz. A signal observed at 6.08-6.23 ppm can be attributed to the aromatic proton in position 7'; it is significantly high field shifted in comparison to the signals of the other protons of the benzene rings (6.68-7.60 ppm) by the known *ortho*-shielding effect of the adjacent methylamino group [12]. The ^{13}C nmr spectra show, besides the resonances of the methyl groups, the C-3' carbon and the *C*-atoms of the benzene rings, the characteristic signals of a quaternary bis-*N*-disubstituted carbon at 92.6-93.1 ppm as well as a carboxylic acid amide carbon at 170.7-171.7 ppm [13]. This carboxylic amide group also causes the ir absorption at 1674-1679 cm^{-1} [14]. A typical feature of the uv spectra is a strong absorption band at 245-263 nm which is accompanied by bands of lower intensity at 307-316 nm and 365-368 nm.

Table 2

Crystal Data Collection Parameters and Structure Refinement Parameters of the Spiro[dihydropyridine-indoline] **5a**

Crystal dimensions (mm^3)		0.40 x 0.20 x 0.05
Measuring temperature (K)		208
Formula		$C_{34}H_{30}N_2O$
M		482.60
Crystal system/Space group		Triclinic/P$\bar{1}$
Unit cell dimensions	a(Å)	8.281(1)
	b (Å)	17.634(2)
	c (Å)	20.227(3)
	α (°)	107.50(1)
	β (°)	94.78(2)
	γ (°)	100.61(2)
V (Å^3)		2738.3(6)
Z		4
D_c (g•cm^{-3})		1.171
F(000)		1024
Data collection method		Omega scans
Linear absorption coefficient (mm^{-1})		0.544
Weighting scheme		$1/[\sigma^2(F_o^2)+(0.1303P)^2+1.0227P]$ with $P = (F_o^2+2F_c^2)/3$
Reflections measured		8462
θ Range (°)		5.14-59.00
Independent reflections/R_{int}		7726/0.1086
R_1(obs.)/R_1(all refl.)		0.0674/0.0822
wR_2(obs.)/wR_2(all refl.)		0.1950/0.2074
Goof (F^2)		1.091
Programs used		SHELXS-97 [21] SHELXL-97 [22]

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ^{1}H nmr and ^{13}C nmr spectra were recorded on a Varian Gemini 200 spectrometer (^{1}H: 199.975 MHz, ^{13}C: 50.289 MHz) and on a Varian Gemini 2000 spectrometer (^{1}H: 200.041 MHz, ^{13}C: 50.305 MHz) in deuteriochloroform or dimethyl-d_6 sulfoxide at 25° with hexamethyl disiloxane as internal standard, ir spectra were obtained on a ATI Mattson Genesis FTIR spectrophotometer (in potassium bromide) and uv 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 1,3-oxazinium salt **1b** [15,16], the 3*H*-indolium salts **3** [3], **4a** ($X^- = ClO_4^-$) [17], the 5-bromo-1,3,3-trimethyl-2-methyleneindoline **2d** [18] and 5-fluoro-2,3,3-trimethylindolenine [19] were synthesized according to literature procedures. The compounds 1,3,3-trimethyl-2-methyleneindoline (**2a**), 5-chloro-1,3,3-trimethyl-2-methyleneindoline (**2c**) and 1,2,3,3-tetramethyl-3*H*-indolium iodide (**4a**, $X^- = I^-$) were purchased from Aldrich.

Preparation of 5-Fluoro-1,2,3,3-tetramethyl-3*H*-indolium Perchlorate (**4b**, $X^- = ClO_4^-$).

5-Fluoro-2,3,3-trimethylindolenine (5.32 g, 30 mmoles) was dissolved in toluene (100 ml). After addition of dimethyl sulfate (3.78 g, 30 mmoles) the reaction mixture was magnetically stirred at 110° for 0.5 hours. The 5-fluoro-1,2,3,3-tetramethyl-3*H*-indolium methosulfate formed as an oil was separated from the toluene solution after cooling by decantation. It was dissolved in ethanol (60 ml) and perchloric acid (70% solution in water,

4.31 g, 30 mmoles) was added dropwise under magnetically stirring. The crystalline precipitate obtained was filtered by suction, washed with ethanol and ether and dried to give 5.14 g (59%) 5-fluoro-1,2,3,3-tetramethyl-3*H*-indolium perchlorate (**4b**, X^- = ClO_4^-) which was used without further purification. A specimen recrystallized from acetonitrile/ether melted at 207-208°; ^1H nmr (dimethyl-d_6 sulfoxide): δ ppm 1.48 (s, 6H, 3-CH_3), 2.69 (s, 3H, 2-CH_3), 3.92 (s, 3H, 1-CH_3), 7.37-7.93 (m, 3H, arom-H).

Anal. Calcd. for $C_{12}H_{15}ClFNO_4$: C, 49.41; H, 5.18; N, 4.80. Found: C, 49.60; H, 5.20; N, 4.86.

Synthesis of 1-Benzoyl-1',3',3'-trimethyl-4,6-diphenylspiro[1,2-dihydropyridine-2,2'-indolines] **5** from 2,4,6-Triphenyl-1,3-oxazinium Tetrafluoroborate (**1b**) and 1,3,3-Trimethyl-2-methyleneindolines **2** or 1,2,3,3-Tetramethyl-3*H*-indolium Salts **4**.

General Procedure.

To absolute acetonitrile (15 ml) 2.5 mmoles indoline **2**, triethylamine (0.25 g, 2.5 mmoles) and 0.99 g (2.5 mmoles) 1,3-oxazinium tetrafluoroborate **1b** were added. The reaction mixture was then refluxed for four hours. If the indolines **2** were generated *in situ* from the corresponding 3*H*-indolium salts **4**, 2.5 mmoles of **4** and 0.50 g (5 mmoles) of triethylamine were added to the absolute acetonitrile. Refluxing was started after magnetically stirring for 0.25 hours at room temperature and addition of **1b.** In both cases the spiro[dihydropyridine-indolines] **5**, thus formed, crystallized upon cooling. They were filtered by suction, washed with ethanol and recrystallized from ethanol/chloroform [20].

1-Benzoyl-1',3',3'-trimethyl-4,6-diphenylspiro[1,2-dihydropyridine-2,2'-indoline] (**5a**).

This compound was obtained according to the general procedure from **1b** and **2a**, from **1b** and **4a** (X^- = I^-) and from **1b** and **4a** (X^- = ClO_4^-) in 41%, 35%, and 36% yield, respectively; mp 155-157°; ^1H nmr (deuteriochloroform): δ 1.29 (s, 3H, 3'-CH_3), 1.77 (s, 3H, 3'-CH_3), 2.81 (s, 3H, 1'-CH_3), 5.76 (d, J = 1.4 Hz, 1H, 3-H), 5.81 (d, J = 1.4 Hz, 1H, 5-H), 6.23 (d, 1H, 7'-H), 6.69-7.60 (m, 18H, arom-H); ^{13}C nmr (deuteriochloroform): δ 22.7 (3'-CH_3), 25.7 (3'-CH_3), 27.7 (1'-CH_3), 51.4 (C-3'), 92.7 (C-2), 101.5, 105.4, 115.7, 118.7, 124.1, 125.5, 125.7, 125.9, 126.0, 126.3, 126.4, 127.0, 127.2, 129.1, 133.9, 135.1, 136.1, 136.6, 137.3, 141.6, 148.0 (olefinic and aromatic carbons), 170.8 (CO); ir: ν 1679 (C=O); uv: λ_{max} (lg ε) 253 (4.52), 307 sh (3.91), 365 (3.71); ms: m/z 482 (7) [M^+], 377 (86) [M^+- PhCO], 105 (100) [$PhCO^+$], 77 (56) [Ph^+].

Anal. Calcd. for $C_{34}H_{30}N_2O$: C, 84.62; H, 6.27; N, 5.80. Found: C, 84.50; H, 6.20; N, 5.86.

1-Benzoyl-5'-fluoro-1',3',3'-trimethyl-4,6-diphenylspiro[1,2-dihydropyridine-2,2'-indoline] (**5b**).

This compound was obtained according to the general procedure from **1b** and **4b** (X^- = ClO_4^-) in 42% yield; mp 183-184°; ^1H nmr (deuteriochloroform): δ 1.28 (s, 3H, 3'-CH_3), 1.75 (s, 3H, 3'-CH_3), 2.78 (s, 3H, 1'-CH_3), 5.74 (d, J = 1.3 Hz, 1H, 3-H), 5.81 (d, J = 1.3 Hz, 1H, 5-H), 6.08 (q, 1H, 7'-H), 6.68-7.60 (m, 17H, arom-H); ^{13}C nmr (deuteriochloroform): δ 22.3 (3'-CH_3), 25.5 (3'-CH_3), 27.9 (1'-CH_3), 51.4 (C-3'), 93.1 (C-2), 100.9, 105.4, 106.9, 110.9, 118.5, 124.1, 125.5, 125.9, 126.1, 126.3, 126.5, 127.0, 127.2, 129.2, 135.3, 135.4, 136.0, 136.5, 137.2, 141.6, 144.3 (olefinic and aromatic carbons), 171.1 (CO); ir: ν 1676 (C=O); uv: λ_{max} (lg ε) 245 (4.51), 316 (3.94), 368 (3.77).

Anal. Calcd. for $C_{34}H_{29}FN_2O$: C, 81.57; H, 5.84; N, 5.60. Found: C, 81.50; H, 5.78; N, 5.50.

1-Benzoyl-5'-chloro-1',3',3'-trimethyl-4,6-diphenylspiro[1,2-dihydropyridine-2,2'-indoline] (**5c**).

This compound was obtained according to the general procedure from **1b** and **2c** in 27% yield; mp 134-136°; ^1H nmr (deuteriochloroform): δ 1.27 (s, 3H, 3'-CH_3), 1.75 (s, 3H, 3'-CH_3), 2.79 (s, 3H, 1'-CH_3), 5.72 (d, J = 1.4 Hz, 1H, 3-H), 5.81 (d, J = 1.4 Hz, 1H, 5-H), 6.11 (d, 1H, 7'-H), 6.93-7.60 (m, 17H, arom-H); ^{13}C nmr (deuteriochloroform): δ 22.4 (3'-CH_3), 25.7 (3'-CH_3), 27.7 (1'-CH_3), 51.4 (C-3'), 92.8 (C-2), 102.1, 105.4, 118.1, 119.4, 120.0, 124.1, 125.3, 125.4, 125.9, 126.1, 126.3, 126.5, 127.0, 127.2, 129.3, 135.4, 135.8, 135.9, 136.5, 137.1, 141.5, 147.5 (olefinic and aromatic protons), 170.9 (CO); ir: ν 1675 (C=O); uv: λ_{max} (lg ε) 263 (4.52), 314 (3.84), 365 (3.69).

Anal. Calcd. for $C_{34}H_{29}ClN_2O$: C, 78.98; H, 5.65; N, 5.42. Found: C, 78.90; H, 5.60; N, 5.38.

1-Benzoyl-5'-bromo-1',3',3'-trimethyl-4,6-diphenylspiro[1,2-dihydropyridine-2,2'-indoline] (**5d**).

This compound was obtained according to the general procedure from **1b** and **2d** in 39% yield; mp 137-138°; ^1H nmr (deuteriochloroform): δ 1.27 (s, 3H, 3'-CH_3), 1.74 (s, 3H, 3'-CH_3), 2.78 (s, 3H, 1'-CH_3), 5.71 (d, J = 1. 3 Hz, 1H, 3-H), 5.81 (d, J = 1.3 Hz, 1H, 5-H), 6.08 (d, 1H, 7'-H), 6.91- 7.59 (m, 17H, arom-H); ^{13}C nmr (deuteriochloroform): δ 22.4 (3'-CH_3), 25.7 (3'-CH_3), 27.7 (1'-CH_3), 51.3 (C-3'), 92.6 (C-2), 105.3, 106.9, 117.5, 117.9, 121.6, 123.9, 125.3, 125.8, 126.0, 126.2, 126.4, 126.9, 127.0, 128.0, 129.1, 135.2, 135.8, 136.1, 136.3, 137.0, 141.4, 147.0 (olefinic and aromatic carbons), 170.7 (CO); ir: ν 1674 (C=O); uv: λ_{max} (lg ε) 261 (4.56), 316 sh (3.95), 365 (3.76).

Anal. Calcd. for $C_{34}H_{29}BrN_2O$: C, 72.73; H, 5.21; N, 4.99. Found: C, 72.70; H, 5.18; N, 4.91.

Preparation of 1-Benzoyl-1',3',3'-trimethyl-4,6-diphenylspiro[1,2-dihydropyridine-2,2'-indoline] (**5a**) from the 3*H*-indolium Dye Salt **3**.

Absolute acetonitrile (5 ml), 0.73 g (1.25 mmoles) of the 3*H*-indolium salt **3** and 0.13 g (1.25 mmoles) triethylamine were refluxed for four hours. The precipitate formed after cooling was filtered by suction and washed with ethanol to give 0.16 g (27%) **5a**; the compound was identical in all respects with those obtained from **1b** and **2a**.

X-Ray Structure Determination.

Appropriate crystals of the spiro[dihydropyridine-indoline] **5a** were obtained by slow cooling of an ethanol/chloroform solution.

The X-ray experiment was carried out on a single crystal diffractometer CAD4 (Enraf Nonius) with graphite-monochromated CuK_α radiation (λ = 1.54184 Å). The structure was solved using direct methods and difference Fourier techniques [21] and refined by a full-matrix least squares procedure on F^2 [22]. Anisotropic displacement parameters have been applied for all non-hydrogen atoms.

More details on data collections and structure determinations are summarized in Table 2. Further details have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 133820.

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.

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