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Spiro Heterocyclic Compound. II.[1] Synthesis of Spiro[indoline-3,3'-(5'-pyrazolin)]-2-ones and Related Compounds

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A spiro-heterocyclate, pyrazole-ring combined at the position-3 of indolin-2-ones was examined.

3-Phenacylideneindolin-2-ones (Ia—d) reacted with hydrazine hydrate to give the corresponding spiro[indoline-3,3'-(5'-pyrazolin)]-2-ones (IIa—d). The reaction of 3-phenacylidene-(Ia) and 3-acetonylideneindolin-2-one (If) with diazomethane afforded 4'-benzoyl- (Va) and 4'-acetyl-spiro[indoline-3,3'-(1'-pyrazolin)]-2-one (Vb), respectively. The decomposition of 1-pyrazolines (Va—b) by thermolysis or by reacting with HCl gave spiro[cyclopropane-1,3'-indolin]-2'-ones (VIa and VIb), whereas during chromatography on alumina changed into 3-(α-benzoyl)- (VIIa) and 3-(α-acetyl)ethylideneindolin-2-one (VIIb), respectively. In addition, 3-(α-nitro)ethylideneindolin-2-one (VIII) reacted with diazomethane to give 1,4'-dimethyl-4'-nitro-spiro[indoline-3,3'-(1'-pyrazolin)]-2-one (IX), which being chromatographed on alumina gave 1,4'-dimethyl-spiro[indoline-3,3'-(3'*H*-pyrazol)]-2-one (X).

In the preceding paper[1] we described the synthesis, for their pharmacological evaluation, of a spiro-heterocyclic system, spiro[imidazolidine-4,3'-indoline]-2,2',5-triones. As a continuation of this series, the present authors investigated on another spiro-heterocyclate which had a pyrazole-ring combined at the position-3 of the 2-indolinone skeleton.

Kobayashi, *et al.*[3] first obtained the spiro[indoline-3,3'-(5'-pyrazoline)] compounds from spiro[indoline-3,2'-oxiran]-2-ones by reacting with hydrazine hydrate. It is also known that the α,β-unsaturated carbonyl system of 3-phenacylideneindolin-2-ones react with dienes and with enamines to give the corresponding spiro-cyclohexane-[4] and spiro-cyclobutane-1,3'-indolin-2-one compounds.[5] These facts suggest that the other ionic addition reactions may take place on the above unsaturated carbonyl system. This paper reports the results obtained by the reactions of some 2-oxo-3-indolylidene compounds with hydrazine hydrate and with diazomethane.

Compounds (Ia—f) were refluxed for 1 hr in methanol with 1.2 molar equivalent of hydrazine hydrate. The analytical and spectral data of the reaction products (IIa—d) were as listed in Table I. In the two cases of Ie and If, the reaction did not proceed as expected, but gave amorphous products.

The ultraviolet (UV) spectra of the compounds (IIa—d) showed no absorption maxima in the visible wave-length region, which suggested a relief of conjugation in the 2-oxo-3-indolylidene system. They showed no carbonyl absorptions due to the acyl groups in the infrared (IR) spectra. The nuclear magnetic resonance (NMR) spectra of IIa—d exhibited a signal of AB-type quartet ($J=18$ Hz) attributable to a methylene protons in the range of 3.3—3.7 ppm. These spectral data along with the elemental analyses are well consistent with the structures of spiro[indoline-3,3'-(5'-pyrazolin)]-2-ones. These compounds reacted with

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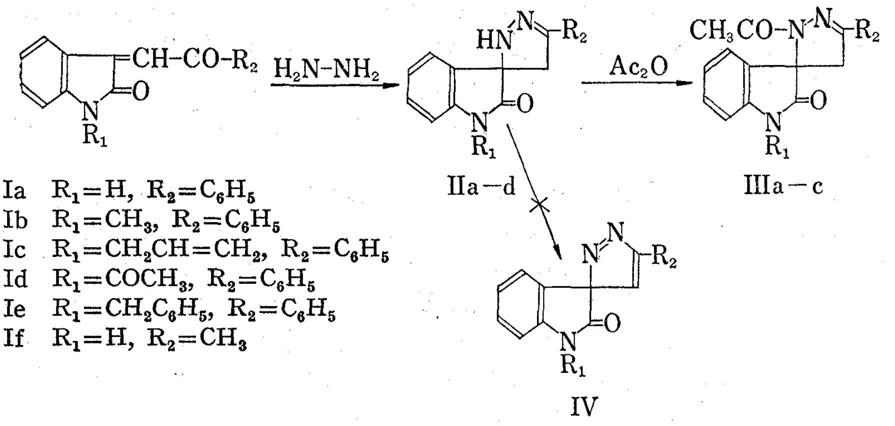
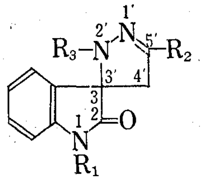
1) Part I: H. Otomasu, K. Natori, and H. Takahashi, *Chem. Pharm. Bull.* (Tokyo), **23**, 1431 (1975).
2) Location: *Ebara, 2-4-41, Shinagawa-ku, Tokyo.*
3) G. Kobayashi, S. Furukawa, and Y. Matsuda, *Yakugaku Zasshi*, **86**, 1156 (1966).
4) T. Kato and H. Ichikawa, *Chem. Pharm. Bull.* (Tokyo), **17**, 481 (1969).
5) G. Tacconi, A. Gamba, F. Marinone, and G. Desimoni, *Tetrahedron*, **27**, 561 (1971).



Ia $R_1=H$, $R_2=C_6H_5$
Ib $R_1=CH_3$, $R_2=C_6H_5$
Ic $R_1=CH_2CH=CH_2$, $R_2=C_6H_5$
Id $R_1=COCH_3$, $R_2=C_6H_5$
Ie $R_1=CH_2C_6H_5$, $R_2=C_6H_5$
If $R_1=H$, $R_2=CH_3$

Chart 1

TABLE I. Spiro[indoline-3,3′-(5′-pyrazolin)]-2-ones



Compd. No.	R_1	R_2	R_3	Yield (%)	mp °C (Solvent)	Formula
IIa	H	C_6H_5	H	70	201($CHCl_3$)	$C_{16}H_{13}ON_3$
IIb	CH_3	C_6H_5	H	63	234(MeOH)[a]	$C_{17}H_{15}ON_3$
IIc	$CH_2CH=CH_2$	C_6H_5	H	61	144(EtOH)	$C_{19}H_{17}ON_3$
IId	$COCH_3$	C_6H_5	H	38	293(MeOH)	$C_{18}H_{15}O_2N_3$
IIIa	H	C_6H_5	$COCH_3$	86	231(MeOH)	$C_{18}H_{15}O_2N_3$
IIIb	CH_3	C_6H_5	$COCH_3$	98	262(EtOH)	$C_{19}H_{17}O_2N_3$
IIIc	$CH_2CH=CH_2$	C_6H_5	$COCH_5$	98	178(EtOH)	$C_{21}H_{19}O_2N_3$

Compd. No.	Analysis (%) Calcd (Found)			IR cm^{-1} (Nujol)		UV λ_{max}^{EtOH} nm (log ε)		
	C	H	N	NH	C=O			
IIa	72.98	4.98	15.96	3300	1700	210	259	296
	(72.65)	(5.02)	(15.90)	3200		(4.32)	(4.12)	(4.20)
IIb	73.64	5.41	15.16	3300	1700	210	263	295
	(73.27)	(4.96)	(15.26)			(4.73)	(4.33)	(4.38)
IIc	75.22	5.65	13.85	3300	1700	211	262	295
	(75.15)	(5.66)	(13.92)			(4.60)	(4.20)	(4.24)
IId	70.80	4.95	13.76	3350	1690	205	255	325
	(70.71)	(5.16)	(13.71)		1645	—	—	—[b]
IIIa	70.80	4.95	13.76	3150	1710			
	(70.76)	(4.65)	(13.61)		1650			
IIIb	71.45	5.37	13.16		1710			
	(71.36)	(5.15)	(12.92)		1650			
IIIc	73.02	5.55	12.17		1710			
	(73.11)	(5.45)	(12.39)		1650			

[a] Recently, it was learned that this compound have been prepared by G. I. Zhungietu, G.A. Dragalina, and G.N. Dorofeenko., *Khim. Geterotsikl. Soedin.*, **1973**, 40; [*C.A.*, **78**, 111201*w* (1973)].
[b] Sparingly soluble and log ε could not be calculated.

acetic anhydride to give the corresponding 2′-acetyl derivatives (IIIa—c). Attempts to dehydrate the pyrazolines to pyrazoles (IV) with the compounds (IIa—d) either by heating with palladized carbon in methanol, or oxidizing with hydrogen peroxide in alkaline solution, or by reacting with bromine in acetic acid, were all unsuccessful and the starting materials were recovered.

Subsequently, in expectation of obtaining the other spiro-system of pyrazole, the reactions of compounds (Ia and If) with diazomethane were carried out. When the solution of Ia or Ie in tetrahydrofuran were allowed to react with excess diazomethane in ether at room temperature, colorless diazomethane adducts, Va or Vb, were produced in excellent yields. Though the largest fragment ion peaks on their mass (MS) spectra appeared each at *m/e* 263 and 201, which are both 28 mass unit less than those of the molecular ions of the presumable formulae (Va and Vb), their analytical values were quite in agreement with the formulae Va and Vb. The NMR spectra of Va and Vb showed the signals for 1H (triplet) and 2H (doubled quartet) protons in the range 3.77—4.49 and 4.90—5.70 ppm as AMX-pattern ($J_{AM}=18$, $J_{AX}=J_{MX}=8$ Hz). From these results, the structures of the adducts were established as 4′-acyl-spiro[indoline-3,3′-(1′-pyrazolin)]-2-ones.

If the reaction involved a nucleophilic attack by the diazomethane carbon on the C-3 of 3-acylmethyleneindolin-2-one, a predominant isomer, spiro[indoline-3,4′-(1′-pyrazoline)] form (V′) would have been obtained. An inspection of the chemical shift of the crude products revealed no evidence for the formation of such isomeric form. These adducts possess a general property characteristic of 1-pyrazolines, that is, they are unstable and decompose slowly in solution at room temperature.

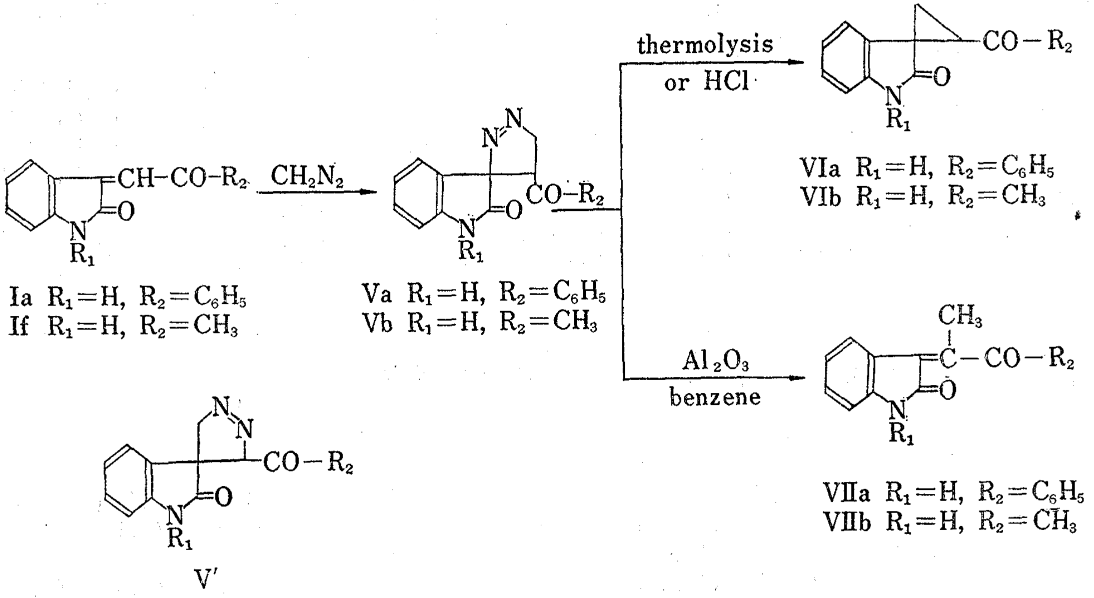


Chart 2

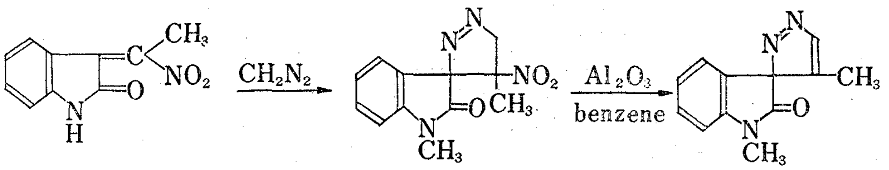
When the dioxane solutions of the adducts Va and Vb were heated at their melting point, gas evolution occurred and colorless products VIa and VIb were obtained in the yields of 80 and 60%, respectively. The products VIa and VIb indicated the molecular ion peaks (M^+) each at *m/e* 263 and 201, showing the loss of the diazo group from Va and Vb. The NMR spectra of VIa and VIb showed the signals for 2H (doubled quartet) and IH (triplet) protons at the region of 1.98—2.53 ppm as AMX-pattern ($J_{AM}=4$, $J_{AX}=J_{MX}=8$ Hz). The chemical shifts for the 2H protons appeared at the higher field than those of the compounds (Va and Vb) and the magnitude of coupling constant was 4 Hz, suggesting that they were cyclopropane derivatives.[6] These results supported the structure of VIa and VIb as 2-benzoyl- and 2-acetyl-spiro[cyclopropane-1,3′-indolin]-2′-one. These spiro-cyclopropane compounds (VIa and VIb) were obtained also by the decomposition of Va and Vb in methanol with conc. hydrochloric acid at room temperature.

Furthermore, the compound Va was subjected to chromatography through a column of alumina by using benzene as a solvent. Thereupon the chromatogram turned yellow with gas evolution, and the eluent gave yellow needles (VIIa) in 57% yield. The M^+ of the product centered at m/e 263. There was seen a singlet of methyl protons at 2.50 ppm in the NMR spectrum, and absorption maximum at 370 nm in the UV spectrum, which suggested the presence of a conjugated 2-indolinone in its structure. In view of the above spectral and analytical data, the structure of VIIa was decided as 3-(α-benzoyl)ethylideneindolin-2-one. Analogous treatment of Vb gave 3-(α-acetyl)ethylideneindolin-2-one (VIIb) as orange needles in 74% yield.

Table II. NMR Spectral Data (ppm, J in Hz, 60 MHz)

IIa	C	3.37, 3.70 (2H, ABq, $J=16$, 4′–CH_2–), 6.75—7.85 (9H, m, arH), 10.29 (1H, s, 1-NH)[a]
IIb	A	3.22 (3H, s, 1-NCH_3), 3.22, 3.72 (2H, ABq, $J=16$, 4′–CH_2–), 6.75—7.77 (9H, m, arH)[a]
IIc	A	3.35, 3.75 (2H, ABq, $J=17$, 4′–CH_2–), 4.29—6.22 (5H, m, N-allyl), 6.76—7.80 (9H, m, arH)[a]
IIIa	C	2.30 (3H, s, $COCH_3$), 3.49, 3.85 (2H, ABq, $J=18$, 4′–CH_2–), 6.78—7.93 (9H, m, arH), 10.65 (1H, s, 1-NH)
IIIb	A	2.40 (3H, s, $COCH_3$), 3.30 (3H, s, 1-NCH_3), 3.42, 3.90 (2H, ABq, $J=17$, 4′–CH_2–), 6.80—7.90 (9H, m, arH)
IIIc	A	2.40 (3H, s, $COCH_3$), 3.40 3.86 (2H, ABq, $J=18$, 4′–CH_2–), 4.30—6.00 (5H, m, N-allyl), 6.80—7.87 (9H, m, arH).
Va	A	4.49 (1H, AMX-type t, $J_{AX}=J_{MX}=8$, 4′–CH–), 5.21, 5.70 (2H, AMX-type dq, $J_{AM}=18$, $J_{AX}=J_{MX}=8$, 5′–CH_2–), 6.68—8.10 (9H, m, arH), 9.32 (1H, s, br, 1-NH)
Vb	B	1.79 (3H, s, 4′–$COCH_3$), 3.77 (1H, AMX-type t, $J_{AX}=J_{MX}=8$, 4′–CH–), 4.90, 5.28 (2H, AMX-type dq, $J_{AM}=18$, $J_{AX}=J_{MX}=8$, 5′–CH_2–), 6.63—7.55 (4H, m, arH), 10.05 (1H, s, br, 1-NH)
VIa	A	2.18, 2.53 (2H, AMX-type dq, $J_{AM}=4$, $J_{AX}=J_{MX}=8$, 3–CH_2–), 3.72 (1H, AMX-type t, $J_{AX}=J_{MX}=8$, 2–CH–), 6.94—8.02 (9H, m, arH), 9.32 (1H, s, br, 1′-NH)
VIb	A	1.98, 2.26 (2H, AMX-type dq, $J_{AM}=4$, $J_{AX}=J_{MX}=8$, 3–CH_2–), 2.21 (3H, s, $COCH_3$), 3.02 (1H, AMX-type t, $J_{AX}=J_{MX}=8$, 2–CH–), 6.80—7.30 (4H, m, arH), 8.70 (1H, s, br, 1-NH)
VIIa	A	2.50 (3H, s, $=\underset{\mid}{C}-CH_3$), 6.60—8.03 (9H, m, arH), 8.54 (1H, s, br, 1-NH)
VIIb	A	2.40 (3H, s, $COCH_3$), 2.52 (3H, s, $=\underset{\mid}{C}-CH_3$), 6.86—7.65 (4H, m, arH), 8.32 (1H, s, br, 1-NH)
IX	A	1.78 (3H, s, 4′–CH_3), 3.29 (3H, s, 1-NCH_3), 4.76, 5.78 (2H, ABq, $J=18$, 5′–CH_2–), 6.92—7.72 (4H, m, arH)
X	A	2.50 (3H, s, 4′–CH_3), 3.72 (3H, s, 1-NCH_3), 7.16—8.03 (5H, m, arH and 5′–CH–)

a) Signal for 2′-NH proton was not observed obviously. IId could not be measured because the sparing solubility.
A: d-chloroform B: d_6-acetone C: d_6-DMSO



VIII IX X

Chart 3

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6) A.A. Bother-By, "Advances in Magnetic Resonance," Vol. 1, Academic Press, New York, 1965, p. 195.

Finally, the reaction of diazomethane with 3-(α-nitro)ethylideneindolin-2-one,[7] the dipolar orientation of which seemed to be analogous to the compound (I), was carried out. The product obtained as colorless needles was determined by its IR, NMR and analytical evidences to be 1,4′-dimethyl-4′-nitro-spiro[indoline-3,3′-(1′-pyrazolin)]-2-one (IX). This compound proved to be somewhat unstable, darkening faintly on standing for several days.

Parham, *et al.*[8] reported that 4-bromo-3-phenyl-4-nitro-2-pyrazoline was converted into 4-bromo-3-phenylpyrazole, releasing nitrous acid, by the treatment with alkaline solution. The same type of the reaction was expected to take place on the product (IX), but the nitropyrazole compound was not obtained.

To purify the compound (IX), a chromatography on alumina employing benzene as a solvent was carried out. The eluent gave a 80% yield of colorless needles of M^+ 213 (X), which apparently differed from the molecular weight of IX. The structure of the product (X) was elucidated as 1,4′-dimethyl-spiro[indoline-3,3′-(3′*H*-pyrazol)]-2-one, from the IR spectrum in which absorption due to nitro group was absent, and from the NMR spectrum where no AB-quartet signal for methylene protons were observed.

However, the stereochemical problem on the compounds, V, VI, and IX, has not been solved yet.

Experimental

All the melting points are uncorrected. IR spectra were recorded with a Hitachi Model-215, UV spectra with a Shimazu UV-200 and Mass spectra with a Hitachi RMS-4 instrument. NMR spectra were determined on a Hitachi-Perkin-Elmer R-20 spectrometer using tetramethylsilane as the internal standard. All evaporation were performed on rotary evaporators *in vacuo*.

Compounds (Ia—f) were prepared according to the method of Lindwall, *et al.*[9]

1-Allyl-3-hydroxy-3-phenacylindolin-2-one——Yield, 94%. Colorless prisms, mp 118° (MeOH). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 3280 (OH), 1680 broad (C=O). *Anal.* Calcd. for $C_{19}H_{17}O_3N$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.19; H, 5.31; N, 4.14.

1-Allyl-3-phenacylideneindolin-2-one (Ic)——Yield, 90%. Red needles, mp 80° (EtOH). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 1700, 1655 (C=O). *Anal.* Calcd. for $C_{19}H_{15}O_2N$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.54; H, 5.02; N, 4.88.

5′-Phenyl-spiro[indoline-3,3′-(5′-pyrazolin)]-2-ones (IIa—d)——In a typical experiment, hydrazine hydrate (0.75 g, 0.015 mole) was added to a solution of Ia (3.0 g, 0.012 mole) in MeOH (60 ml), and refluxed for 1 hr. After evaporation of MeOH, the residue was rinsed with $CHCl_3$ and the insoluble solid was recrystallized from $CHCl_3$ to give colorless needles of mp 201°.

2′-Acetyl-5′-phenyl-spiro[indoline-3,3′-(5′-pyrazolin)]-2-ones (IIIa—c)——Compounds (IIa—c) were acetylated with Ac_2O in an usual manner. The products (IIIa—c) obtained are listed in Table I.

4′-Benzoyl-spiro[indoline-3,3′-(1′-pyrazolin)]-2-one (Va)——To a solution of Ia (5.0 g) in tetrahydrofuran (THF) (80 ml) was added an ether solution (120 ml) of diazomethane (prepared from 6 g of nitrosomethylurea) in the period of 20 min under ice-cooling and stirring. The mixture was kept standing at room temperature for 6 hr, the solvent was evaporated below 40° and the residual solid was washed with ether. Yield 5.3 g, 92%. Recrystallization from acetone and ether to give colorless prisms of mp 116—118° (decomp.). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 3300 (NH), 1730, 1680 (C=O). Mass Spectrum *m/e*: 263 (M^+-28). *Anal.* Calcd. for $C_{17}H_{13}O_2N_3$: C, 70.09; H, 4.50; N, 14.43. Found: C, 69.95; H, 4.41; N, 14.46.

4′-Acetyl-spiro[indoline-3,3′-(1′-pyrazolin)]-2-one (Vb)——To a solution of If (4.0 g) in THF (60 ml) was added an ether solution (100 ml) of diazomethane (prepared from 5 g of nitrosomethylurea) under ice-cooling and stirring. The mixture was worked up in the manner described above and crude Vb was obtained in 90% yield. Recrystallization from acetone and ether to give colorless prisms, mp 110° (decomp.). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 3150 (NH), 1720—1695 (C=O). Mass Spectrum *m/e*: 201 (M^+-28). *Anal.* Calcd. for $C_{12}H_{11}O_2N_3$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.58; H, 4.52; N, 18.72.

2-Benzoyl-spiro[cyclopropane-1,3′-indolin]-2′-one (VIa)——i) Thermal Treatment of Va: A solution of Va (1.0 g) in dioxane (10 ml) was heated at 120° for 2 hr with stirring. Evaporation of dioxane gave 0.72 g (80%) of crude VIa. Recrystallization from benzene to give colorless needles, mp 193—194°. IR $\nu_{\text{max}}^{\text{Nujol}}$

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[7] H. Otomasu, K. Yoshida, and K. Natori, *Chem. Pharm. Bull.* (Tokyo), **23**, 1436 (1975).

[8] W.E. Parham and J.L. Bleasdale, *J. Am. Chem. Soc.*, **72**, 3843 (1950); *idem, ibid.*, **73**, 4664 (1951).

[9] H.G. Lindwall and J.S. Maclennan, *J. Am. Chem. Soc.*, **54**, 4739 (1932); F. Braude and H.G. Lindwall, *ibid.*, **55**, 325 (1933).

cm^{-1}: 3190 (NH), 1705, 1665 (C=O). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 209 (4.57), 250 (4.38), 282 s (3.62), 313 s (3.30). Mass Spectrum m/e: 263 (M$^+$). *Anal.* Calcd. for $C_{17}H_{13}O_2N$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.45; H, 4.82; N, 5.49.

ii) Hydrochloric Acid Treatment of Va: To a solution of Va (0.4 g) in MeOH (20 ml) was added conc. HCl (1 ml) dropwise at room temperature with stirring. After the gas evolution ceased, evaporation of the solvent gave 0.36 g (83%) of crude VIa. Recrystallization from benzene to give colorless needles, identical with the above sample.

2-Acetyl-spiro[cyclopropane-1,3′-indolin]-2′-one (VIb)——A solution of Vb (1.0 g) in dioxane (10 ml) was worked up in the manner described for Va. Evaporation of dioxane gave 0.52 g (60%) of crude VIb. Recrystallization from benzene to give colorless needles of mp 189°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3170 (NH), 1715—1695 (C=O). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 204 (4.27), 228 (4.33), 261 (3.76), 297 (3.32). Mass Spectrum m/e: 201 (M$^+$). *Anal.* Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51; N, 6.96. Found: C, 72.02; H, 5.43; N, 7.06.

This compound was also obtained in 74% yield by the HCl treatment of Vb in the manner described for Va.

3-(α-Benzoyl)ethylideneindolin-2-one (VIIa)——Va (1.0 g) was dissolved in 100 ml of benzene containing a small amount of dioxane without heating, and the solution was run through the column packed with Al_2O_3 (Merck, Art 1097, 2.1 × 12 cm). The elution with benzene gave 0.51 g (57%) of VIIa. Recrystallization from benzene to give yellow needles of mp 188°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3150 (NH), 1710, 1665 (C=O). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 204 (4.46), 253 (4.60), 293 (3.88), 370 (3.02). Mass Spectrum m/e: 263 (M$^+$). Anal. Calcd. for $C_{17}H_{13}O_2N$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.64; H, 4-78; N, 5.61.

3-(α-Acetyl)ethylideneindolin-2-one (VIIb)——A CH_2Cl_2 solution of Vb was worked up in the manner described above. The elution with CH_2Cl_2 gave a 74% yield of VIIb as orange needles of mp 171° (benzene). IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3175 (NH), 1695, 1675 (C=O). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 201 (4.17), 256 (4.43), 295 (3.61), 370 (3.02). Mass Spectrum m/e: 201 (M$^+$). *Anal.* Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51; N, 6.96. Found: C, 72.03; H, 5.47; N, 6.81.

1,4′-Dimethyl-4′-nitro-spiro[indoline-3,3′-(1′-pyrazolin)]-2-one (IX)——A solution of VIII (2.5 g) in THF (40 ml) was added an ether solution (80 ml) of diazomethane (prepared from 5 g of nitrosomethylurea) in a similar manner as described for V. After the mixture was kept standing over night at room temperature, the solvent was removed below 40°, and the residual solid was washed with a mixt. of benzene and ligroin (1: 1). Yield 1.7 g, 55%. Recrystallization from benzene to give colorless needles of mp 134° (decomp.). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1720 (C=O), 1550, 1345 (NO_2). *Anal.* Calcd. for $C_{12}H_{12}O_3N_4$: C, 55.38; H, 4.65; N, 21.53. Found: C, 55.77; H, 4.21; N, 21.78.

1,4′-Dimethyl-spiro[indoline-3,3′-(3′*H*-pyrazol)]-2-one (X)——A solution of IX (0.78 g) in benzene (60 ml) was run through the column of alumina (Merck, Art 1097, 2.1 × 15 cm). The first elution with benzene gave a small amount of tary substance. The second elution with a mixt. of benzene and MeOH (1: 1) gave 0.5 g (82%) of white solid. Recrystallization from benzene to give colorless needles of mp 226—228°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 1705 (C=O). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 202 (4.03), 228 (4.60), 264 (4.13), 279 (4.03), 311 (4.12), 324 (4.15). Mass Spectrum m/e: 213 (M$^+$). *Anal.* Calcd. for $C_{12}H_{11}ON_3$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.21; H, 4.99; N, 19.75.