Reactions 1-Acetyl-3-oxo-2,3-dihydroindole with Alkyl 2-Cyano-3-alkoxypropenoate and Alkyl 2-Alkoxycarbonyl-3-alkoxypropenoate. Synthesis of 9-Acetoxypyrrolo[1,2-*a*]indol-3-one Derivatives

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1-Acetyl-3-oxo-2,3-dihydroindole reacted with methyl 2-cyano-3-methoxypropenoate and ethyl 2-cyano-3-ethoxypropenoate in the presence of sodium hydride, affording compounds **3** (2-(2-cyano-2-alkoxycarbonyl-vinyl)-3-hydroxyindole). Methyl 2-methoxycarbonyl-3-methoxypropenoate gave compounds **4** or compounds **5** (in the presence of Triton B). Heating compounds **3** or their acetylated derivatives in acetic anhydride at reflux afforded 9-acetoxy-(3*H*)-pyrrolo[1,2-*a*]indol-3-one **8**.

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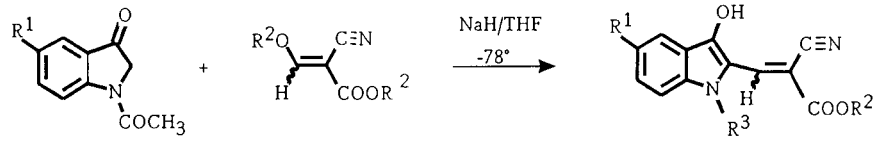
Our interest in the reactivity of 1-acetyl-3-oxo-2,3-dihydroindole **1** [1-3] led us to examine its behaviour towards alkyl 2-cyano-3-alkoxypropenoate **2**. The higher reactivity of the 2 position was born out by numerous chemical evidences [4,5]. Alkoxy groups in compounds **2** were rapidly substituted by nucleophilic reagents [6].

1-Acetyl-3-oxo-2,3-dihydroindole **1a** reacted with methyl 2-cyano-3,3-dimethylthiopropenoate affording 1-acetyl-2-(2-cyano-2-methoxycarbonyl-1-methylthiovinyl)-3-hydroxyindole as described [7]. Compounds **1a** and **1b** (5-methoxy-1-acetyl-3-oxo-2,3-dihydroindole) reacted with methyl 2-cyano-3-methoxypropenoate **2a** and ethyl 2-cyano-3-ethoxy-

Figure 1

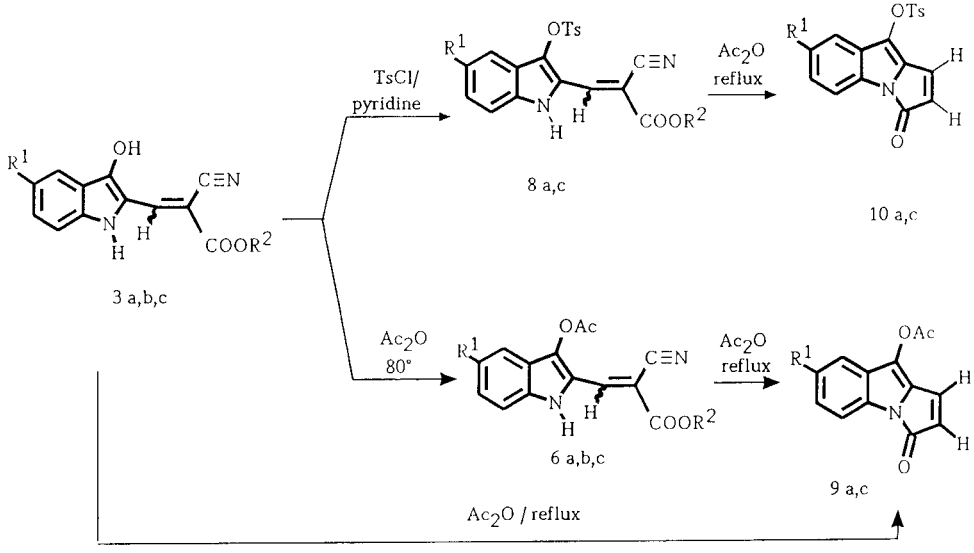


1a R^1 = H
1b R^1 = OCH_3

2a R^2 = CH_3
2b R^2 = C_2H_5

	R^1	R^2	R^3
3a	H	CH_3	H
3b	H	C_2H_5	H
3c	OCH_3	CH_3	H

Figure 2



3 a,b,c

8 a,c

10 a,c

6 a,b,c

9 a,c

propenoate **2b** for giving compounds **3** as a mixtue of *E* + *Z* isomers.

The reactions were performed in the presence of 1 or 2 equivalents of sodium hydride in tetrahydrofuran at low temperature −78°; at 0° only tarry products were obtained. No cyclization to compounds having the pyrano or pyrrolo structure was observed; pyrano compounds have been obtained with chromanones [8] with 3-oxo-2,3-dihydrobenzofuran [9] (in some cases) and tetralones [10]. Pyrrolo compounds have been obtained with **1** and ketenethioacetal [7] in presence of 2 equivalents of sodium hydride.

The use of Triton B (40% in methanol), as base, gave also compounds **3** with similar or decreased yields. Using potassium carbonate in dimethylformamide instead of sodium hydride afforded a mixture of compounds **3** (R^3 = H, no acetyl group on the nitrogen indolic atom) and compounds **15** (R^3 = $COCH_3$, acetyl group on the nitrogen indolic atom).

The structure of compounds **3** were confirmed by *O*-acetylation with an excess of acetic anhydride at 80° in the presence of sodium acetate; products **6** were obtained as a mixture of *E* + *Z* isomers which were easily distinguished by nmr spectroscopy and partially separated by flash chromatography; acetylation of the indole nitrogen atom for giving diacetylated compound was observed only as traces of compounds **7** (<5%) (these compounds **7** were easily obtained by *O*-acetylation of compounds **15** in the mixture of compounds **15** and **3**). Compounds **3** were also tosylated with *p*-toluenesulfonyl chloride giving compounds **8** (*E* + *Z* mixture of isomers which were separated for compound **8c**).

Compounds **6** or **8** in refluxing acetic anhydride (5 hours) afforded the cyclized product **9** or **10**, with a pyrrolo structure, where the cyano group has been lost. Compound **9** could also be directly obtained from compound **3** by refluxing acetic anhydride in the presence of sodium acetate and compound **3**.

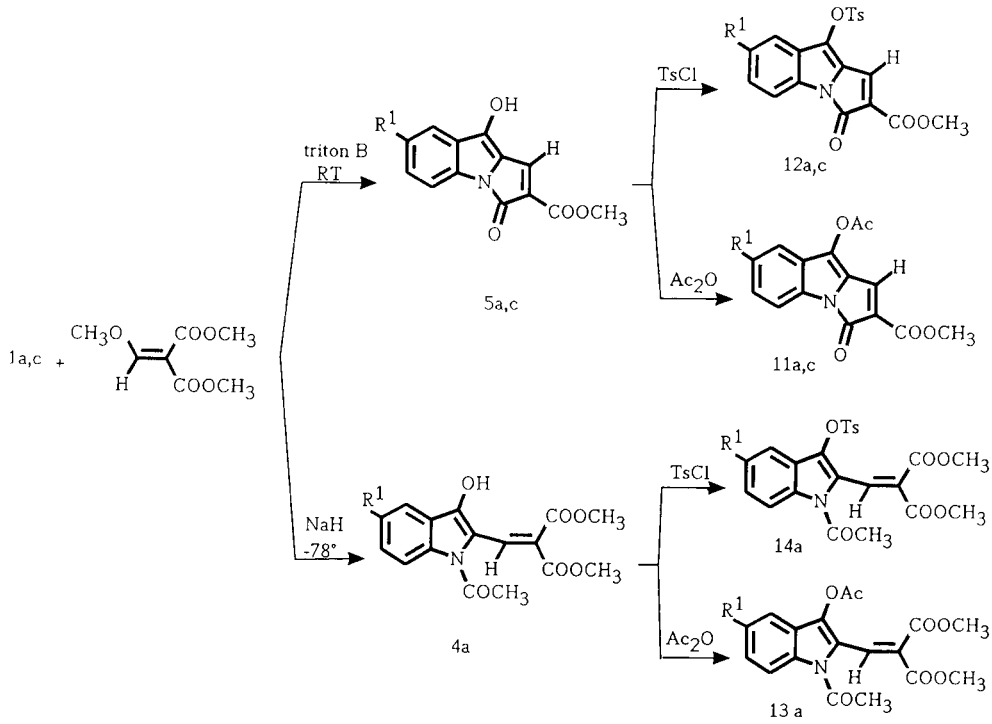
Methyl 2-methoxycarbonyl-3-methoxypropenoate as opposed to compound **1a** in the presence of 2 equivalents of sodium hydride in tetrahydrofuran at −78° afforded compound **4a** as the major product (70%) accompanied by unreacted compound **1a** and unidentified products in the crude oil which decomposed on silica gel. The structure of compound **4a** was indirectly established by acetylation and tosylation at room temperature, affording compounds **13a** and **14a**.

The use of Triton B in excess, at room temperature, instead of sodium hydride afforded directly the cyclized compound **5** with the pyrrolo structure.

In order to confirm this structure, reactions of compounds **5** with acetic anhydride or tosyl chloride were performed at room temperature, in order to prevent any cyclization, giving respectively compound **11** and **12**.

In the 3-oxo-2,3-dihydrobenzofuran series [9] 2-dimeth-

Figure 3



ylaminomethylene-3-oxo-2,3-dihydrobenzofurans were prepared by reaction of 3-oxo-2,3-dihydrobenzofuran with *N,N*-dimethylformamide diethylacetal. This reaction did not occur with compound **1a** so compounds **3** could not be obtained by this route (displacement of the dimethylamino moiety with methyl cyanoacetate).

Compounds **1** reacted in a different way with alkyl 2-alkoxycarbonyl-3-alkoxypropenoate or compounds **2**; in the first case pyrrolo compounds **5** were directly obtained; with compounds **2** it was necessary to reflux in acetic anhydride compounds **3**, first obtained, in order to afford cyclized compounds **10**. Compounds **5** were synthetically interesting due to their high degree of functionality.

EXPERIMENTAL

Melting points (uncorrected) were determined on a Kofler apparatus. The ir spectra were obtained with a Perkin-Elmer 257 spectrophotometer; the ^{1}H nmr spectra were recorded with deuteriochloroform as the solvent on a Bruker model AM 300 WB (300 MHz) spectrometer with tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million and signals are quoted as s (singlet), d (doublet), fd (false doublet), t (triplet), q (quartet), m (multiplet). Mass spectra were determined with a Nermag R10-10C mass spectrometer.

2-(2-Cyano-2-alkoxycarbonylvinyl)-3-hydroxyindole (**3**). General Procedure.

Method A.

A solution of compound **1** (5 mmoles) in tetrahydrofuran (30 ml) was dropwise added (15 minutes), under nitrogen, to a suspension of sodium hydride (11 mmoles) in tetrahydrofuran (20 ml) cooled at −78°. The mixture was stirred 30 minutes; the alkyl 2-cyano-3-alkoxypropenoate **2** (5.5 mmoles) in tetrahydrofuran (20 ml) was dropwise added (15 minutes) at −78° and the mixture was stirred 18 hours at room temperature. Water (100 ml) was added and the mixture acidified with dilute hydrochloric acid to *p*H 1. A solid precipitated which was recrystallized in ethanol or methanol.

Method B.

To a solution of compound **1** (9 mmoles) and methyl 2-cyano-3-methoxypropenoate **2a** (10 mmoles) in methanol (25 ml) under nitrogen and cooled by an ice bath, Triton B (40% in methanol) (16 mmoles) was dropwise added and the mixture was stirred 20 hours at room temperature. Water (250 ml) was added and the mixture was acidified with dilute hydrochloric acid to *p*H 3; a solid precipitated and was recrystallized from methanol.

2-(2-Cyano-2-methoxycarbonylvinyl)-3-hydroxyindole (**3a**).

This compound was obtained according method A in 72% yield, mp 210°; ir (potassium bromide): 3350 (OH), 2230 (CN), 1685 (CO) cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): 3.80 (s, 3H, OC*H*$_3$), 6.8-8.2 (m, 5H, *H* arom, O*H*), 8.25 (s, 1H, =C*H*), 9.8 (br s, 1H, N*H*); ms: (m/e) 242 (M$^+$).

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.29; H, 4.35; N, 11.69.

2-(2-Cyano-2-ethoxycarbonylvinyl)-3-hydroxyindole (**3b**).

This compound was obtained according method A in 60% yield, mp 238°; ir (potassium bromide): 3350 (OH), 2240 (CN), 1670 (CO) cm^{-1}; ^{1}H nmr (deuteriochloroform): 1.30 (t, J = 7, 3H, C*H*$_3$), 4.25 (q, J = 7, 2H, OC*H*$_2$), 6.9-8.2 (m, 5H, *H* arom, OH), 8.25 (s, 1H, =C*H*), 9.8 (br s, 1H, N*H*); ms: (m/e) 256 (M$^+$).

Anal. Calcd. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.81; H, 4.58; N, 11.04.

1-Acetyl-2-(2,2-dialkoxycarbonylvinyl)-3-hydroxyindole (**4**).

Same procedure (method A) as for compound **3** using methyl 2-methoxycarbonyl-3-methoxypropenoate (0.95 equivalent) instead of alkyl 2-cyano-3-alkoxypropenoate was employed. Extraction with dichloromethane (2 x 100 ml) and drying over magnesium sulfate afforded after evaporation an oil which decomposed on a silica gel column. The crude oil was a mixture of compound **4** as the major component (65%-80%), unreacted compound **1** and other unidentified products; ir (neat): 3300 (OH), 1710 and 1650 (CO) cm^{-1} (crude oil).

2-Methoxycarbonyl-9-hydroxy-3*H*-pyrrolo[1,2-*a*]indol-3-one (**5a**).

To a suspension of compound **1a** (1.75 g, 10 mmoles) and methyl 2-methoxycarbonyl-3-methoxypropenoate (1.65 g, 9.5 mmoles) in methanol (25 ml) Triton B (40% in methanol) (8 ml, 17.6 mmoles) in methanol (10 ml) was dropwise added at room temperature under nitrogen; the mixture was stirred 32 hours, evaporated *in vacuo* and the residue treated with water (200 ml) and acidified to *p*H 3 with dilute hydrochloric acid to leave a black solid which was recrystallized from methanol (brown solid), yield 1.25 g (54%), mp 215°; ir (potassium bromide): 3300 (OH), 1695 and 1645 (CO) cm^{-1}; ^{1}H nmr (pyridine-d_5): 3.10 (s, 3H, OC*H*$_3$); ms: (m/e) 243 (M$^+$).

2-Methoxycarbonyl-7-methoxy-9-hydroxy-3*H*-pyrrolo[1,2-*a*]indol-3-one (**5c**).

Same procedure as for compound **5a** starting from compound **1b** gave a yield of 45%, mp 210° dec; ir (potassium bromide): 3300 (OH), 1720 (CO) cm^{-1}; ms: (m/e) 273 (M$^+$).

For compound **5a,c** no satisfactory microanalyses were obtained.

2-(2-Cyano-2-alkoxycarbonylvinyl)-3-acetoxyindole (**6**). General Procedure.

Compound **3** (5 mmoles), acetic anhydride (15 mmoles), sodium acetate (10 mmoles) were stirred at 80° for 1 hour. After evaporation of the excess acetic anhydride *in vacuo* the residue was treated with water (50 ml) and extracted with dichloromethane (2 x 50 ml); drying of the organic extracts and evaporation afforded a solid which was chromatographed on a silica gel column (230/400 mesh) using dichloromethane as the eluent.

2-(2-Cyano-2-methoxycarbonylvinyl)-3-acetoxyindole (**6a**).

This compound was obtained in 68% yield, mp 192°; ir (potassium bromide): 3350 (NH), 2215 (CN), 1750 and 1710 (CO) cm^{-1}; ^{1}H nmr (deuteriochloroform): 2.47 (s, 3H, C*H*$_3$), 3.90 (s, 3H, OC*H*$_3$), 7.15 (m, 2H, *H* arom), 7.38 (fd, J = 4.4, 1H, *H* arom), 7.44 (fd, J = 8.8, 1H, *H* arom), 8.10 (s, 1H, =CH), 9.32 (s, 1H, N*H*), *E* isomer, 2.48 (s, 3H, C*H*$_3$), 3.92 (s, 3H, OC*H*$_3$), 11.4 (s, 1H, N*H*), *Z* isomer; ms: (m/e) 284 (M$^+$).

Anal. Calcd. for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.52; H, 4.37; N, 9.80.

2-(2-Cyano-2-ethoxycarbonylvinyl)-3-acetoxyindole (**6b**).

This compound was obtained in 50% yield; mp 170°; ir (potassium bromide): 3320 (NH), 2220 (CN), 1760 and 1710 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 1.42 (t, J = 7.3, 3H, CH_3), 2.48 (s, 3H, $COCH_3$), 4.39 (q, J = 7.3, 2H, OCH_2), 7.15-7.21 (m, 2H, *H* arom), 7.38-7.49 (m, 2H, *H* arom), 8.14 (s, 1H, =C*H*), 9.28 (s, 1H, N*H*), *E* isomer; 1.43 (t, J = 7.3, 3H, CH_3), 7.29 (s, 1H, =C*H*), 11.4 (s, 1H, N*H*), *Z* isomer; ms: (m/e) 298 (M^+).

Anal. Calcd. for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.32; H, 4.87; N, 9.21.

2-(2-Cyano-2-methoxycarbonylvinyl)-3-acetoxy-5-methoxyindole (**6c**).

This compound was obtained in 76% yield, mp 222°; ir (potassium bromide): 3400 (NH), 2210 (CN), 1750 and 1720 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.48 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 3.92 (s, 3H, $COOCH_3$), 6.70 (dd, J = 2.8, 9, 1H, *H* arom) [11], 7.05-7.11 (m, 1H, *H* arom) [11], 7.29 (fd, J = 9, 1H, *H* arom), 8.05 (s, 1H, =CH), 9.25 (s, 1H, N*H*), *E* isomer; 2.49 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 3.95 (s, 3H, $COOCH_3$), 7.24 (fd, J = 5, 1H, *H* arom), 7.48 (s, 1H, =C*H*), 11.4 (s, 1H, N*H*), *Z* isomer; ms: (m/e) 314 (M^+).

Anal. Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.91. Found: C, 61.27; H, 4.75; N, 8.84.

1-Acetyl-2-(2-cyano-2-methoxycarbonylvinyl)-3-acetoxyindole (**7a**).

Same procedure as for compound **6a** starting from a mixture of compounds **3a** and **15a** was applied. The solid was chromatographed on a silica column (230/400 mesh) using dichloromethane as eluent; compound **6a** was first eluted and then compound **7a**, yield 55% (based on the ratio **6a**/**15a** in the original mixture), mp 178°; ir (potassium bromide): 2220 (CN), 1750 large (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.50 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 3.93 (s, 3H, OCH_3), 7.33 (ft, J = 8.3, 1H, *H* arom), 7.5 (m, 2H, *H* arom), 7.84 (fd, J = 8.3, 1H, *H* arom), 8.44 (s, 1H, =C*H*), *E* isomer; 2.35 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 7.43 (fd, J = 7.1, 1H, *H* arom), 7.50 (m, 2H, *H* arom), 7.76 (s, 1H, =C*H*), 7.82 (fd, J = 8.3, 1H, *H* arom), *Z* isomer; ms: (m/e) 326 (M^+).

Anal. Calcd. for $C_{17}H_{14}N_2O_5$: C, 62.58; H, 4.32; N, 8.58. Found: C, 62.79; H, 4.52; N, 8.33.

2-(2-Cyano-2-alkoxycarbonylvinyl)-3-*p*-toluenesulfonyloxyindole (**8**). General Procedure.

Compounds **3** (5 mmoles), tosyl chloride (7.5 mmoles), pyridine (100 mmoles) were stirred 24 hours in dichloromethane (25 ml) at room temperature. Water (150 ml) was added and after decantation the aqueous layer was extracted with dichloromethane (75 ml); the organic layers were washed successively with dilute hydrochloric acid (50 ml) and water (50 ml). Evaporation of the dichloromethane solution, after drying over magnesium sulfate, afforded a solid which was chromatographed on a silica gel column (230/400 mesh) using dichloromethane as eluent.

2-(2-Cyano-2-methoxycarbonylvinyl)-3-*p*-toluenesulfonyloxyindole (**8a**).

This compound was obtained in 59% yield, mp 182°; ir (potassium bromide): 3360 (NH), 2220 (CN), 1700 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.44 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 7.1-7.6 (m, 8H, *H* arom), 7.70 (s, 1H, = C*H*), 9.34 (s, 1H, N*H*), *E* isomer; 2.50 (s, 3H, CH_3), 3.95 (s, 3H, OCH_3), 7.1-7.6 (m, 8H, *H* arom), 7.38 (s, 1H, =C*H*), 11.4 (s, 1H, N*H*), *Z* isomer; ms (m/e) 396 (M^+).

Anal. Calcd. for $C_{20}H_{16}N_2O_5S$: C, 60.60; H, 4.07; N, 7.07. Found: C, 60.31; H, 4.26; N, 7.18.

2-(2-Cyano-2-methoxycarbonylvinyl)-3-*p*-toluenesulfonyloxy-5-methoxyindole (**8c**).

This compound was obtained in 54% yield, mp 184° (*E* isomer), 200° (*Z* isomer); ir (potassium bromide): 3280 (NH), 2215 (CN), 1700 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.50 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.76 (fd, J = 2.5, 1H, *H*4 arom), 7.06 (dd, J = 2.4, 9.5, 1H, *H*6 arom), 7.25 (fd, J = 9.5, 1H, *H*7 arom), 7.38 (fd, J = 9.5, 2H, *H* arom), 7.66 (s, 1H, =C*H*), 7.74 (fd, J = 9.5, 2H, *H* arom), 9.27 (s, 1H, N*H*), *E* isomer; 2.43 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.70 (fd, J = 2.4, 1H, *H* arom), 6.80 (s, 1H, =C*H*), 7.06 (dd, J = 9.5, 2.4, 1H, *H* arom), 7.25 (fd, J = 9.5, 1H, *H* arom), 7.33 (fd, J = 8.4, 2H, *H* arom), 7.74 (fd, J = 8.4, 2H, *H* arom), 11.4 (s, 1H, N*H*), *Z* isomer; ms: (m/e) 426 (M^+).

Anal. Calcd. for $C_{21}H_{18}N_2O_6S$: C, 59.15; H, 4.25; N, 6.57. Found: C, 59.43; H, 4.12; N, 6.34.

9-Acetoxy-3*H*-pyrrolo[1,2-*a*]indol-3-one (**9a**).

Same procedure as for compound **6a**, starting with compound **6a** or compound **3a**, but with 5 hours reflux of acetic anhydride was employed. This compound was obtained from **6a** in 52% yield, mp 112°; ir (potassium bromide): 1770 and 1690 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.37 (s, 3H, CH_3), 5.88 (d, J = 5.5, 1H, =CH_2), 7.07 (ft, J = 8, 1H, *H*7 arom), 7.27 (ft, J = 8, 1H, *H*6 arom), 7.34 (fd, J = 8, 1H, *H*8 arom), 7.37 (d, J = 5.5, 1H, =C*H*1), 7.65 (fd, J = 8, 1H, *H*5 arom); ms: (m/e) 227 (M^+).

Anal. Calcd. for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16. Found: C, 68.53; H, 4.05; N, 6.21.

7-Methoxy-9-acetoxy-3*H*-pyrrolo[1,2-*a*]indol-3-one (**9c**).

This compound was similarly obtained from **6c** in 73% yield; mp 140°; ir (potassium bromide): 1760 and 1690 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.38 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 5.86 (d, J = 5.5, 1H, =CH_2), 6.82 (fd, J = 2.8, 1H, *H*8 arom), 6.87 (dd, J = 2.8, 8.7, 1H, *H*6 arom), 7.34 (d, J = 5.5, 1H, =C*H*1), 7.54 (fd, J = 8.7, 1H, *H*5 arom); ms: (m/e) 257 (M^+).

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.44. Found: C, 65.42; H, 4.39; N, 5.47.

9-(*p*-Toluenesulfonyloxy)-3*H*-pyrrolo[1,2-*a*]indol-3-one (**10a**).

Same procedure as for compound **9a** starting from compound **8a** was employed. This compound was obtained in 59% yield, mp 142°; ir (potassium bromide): 1725 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.42 (s, 3H, CH_3), 5.94 (d, J = 5.4, 1H, =CH_2), 6.9-7.1 (m, 2H, *H* arom), 6.99 (d, J = 5.4, 1H, =C*H*1), 7.2 (m, 1H, *H* arom), 7.28 (fd, J = 8.2, 2H, *H* arom), 7.59 (fd, J = 8.2, 1H, *H*5 arom), 7.77 (fd, J = 8.2, 2H, *H* arom), ms: (m/e) 339 (M^+).

Anal. Calcd. for $C_{18}H_{13}NO_4S$: C, 63.71; H, 3.86; N, 4.13. Found: C, 63.98; H, 3.95; N, 4.08.

7-Methoxy-9-(*p*-toluenesulfonyloxy)-3*H*-pyrrolo[1,2-*a*]indol-3-one (**10c**).

This compound was similarly obtained from **8c** in 52% yield; mp 172°; ir (potassium bromide): 1720 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.45 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 5.88 (d, J = 6.2, 1H, =CH_2), 6.48 (fd, J = 3, 1H, *H*8 arom), 6.83 (dd, J = 3, 8.5, 1H, *H*6 arom), 6.93 (d, J = 6.2, 1H, =C*H*1), 7.34 (fd, J = 8.5,

2H, *H* arom), 7.49 (fd, J = 8.5, 1H, *H*5 arom), 7.83 (fd, J = 8.5, 2H, *H* arom); ms: (m/e) 369 (M^+).

Anal. Calcd. for $C_{19}H_{15}NO_5S$: C, 61.78; H, 4.09; N, 3.79. Found: C, 61.98; H, 4.20; N, 3.87.

2-Methoxycarbonyl-9-acetoxy-3*H*-pyrrolo[1,2-*a*]indol-3-one (**11a**).

Compound **5a** (1.21 g, 5 mmoles), acetic anhydride (15 ml, 158 mmoles) and sodium acetate (0.82 g, 10 mmoles) were stirred 1 day at room temperature; the residue obtained after evaporation, *in vacuo*, of the excess of acetic anhydride was treated with water (50 ml) and dichloromethane (2 x 50 ml). The organic layers were washed with water (50 ml) and dried over magnesium sulfate; the solid obtained after evaporation of the solvent was chromatographed on a silica gel column (230/400 mesh) using dichloromethane as eluent to afford **11a**, yield 0.71 g (50%); mp 200°; ir (potassium bromide): 1770 and 1735 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.44 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 7.15 (ft, J = 7.9, 1H, *H* arom), 7.39 (ft, J = 7.9, 1H, *H* arom), 7.45 (fd, J = 7.9, 1H, *H* arom), 7.76 (fd, J = 7.9, 1H, *H* arom), 8.16 (s, 1H, =C*H*); ms: (m/e) 285 (M^+).

Anal. Calcd. for $C_{15}H_{11}NO_5$: C, 63.16; H, 3.89; N, 4.91. Found: C, 63.47; H, 4.03; N, 4.72.

2-Methoxycarbonyl-7-methoxy-9-acetoxy-3*H*-pyrrolo[1,2-*a*]indol-3-one (**11c**).

This compound was obtained in 47% yield, mp 182°; ir (potassium bromide): 1760 and 1725 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.42 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.84 (fd, J = 3, 1H, *H*8 arom), 6.99 (dd, J = 3, 8.9, 1H, *H*6 arom), 7.65 (fd, J = 8.9, 1H, *H*5 arom), 8.13 (s, 1H, =C*H*); ms: (m/e) 315 (M^+).

Anal. Calcd. for $C_{16}H_{13}NO_6$: C, 60.95; H, 4.16; N, 4.44. Found: C, 61.26; H, 4.30; N, 4.27.

2-Methoxycarbonyl-9-*p*-toluenesulfonyloxy-3*H*-pyrrolo[1,2-*a*]-indol-3-one (**12a**).

Same procedure as for compound **8** starting from compound **5** was employed. This compound was obtained in 30% yield, mp 201°; ir (potassium bromide): 1750 large (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.46 (s, 1H, CH_3), 3.89 (s, 3H, OCH_3), 7.05 (ft, J = 8.2, 2H, *H* arom), 7.15 (fd, J = 8.2, 1H, *H* arom), 7.35 (fd, J = 8.2, 2H, *H* arom), 7.67 (s, 1H, =C*H*), 7.71 (fd, J = 8.2, 1H, *H* arom), 7.82 (fd, J = 8.2, 2H, *H* arom); ms: (m/e) 397 (M^+).

Anal. Calcd. for $C_{20}H_{15}NO_6S$: C, 60.45; H, 3.80; N, 3.52. Found: C, 60.32; H, 3.71; N, 3.80.

2-Methoxycarbonyl-7-methoxy-9-*p*-toluenesulfonyloxy-3*H*-pyrrlo-[1,2-*a*]indol-3-one (**12c**).

This compound was obtained from compound **5** in 68% yield, mp 212°; ir (potassium bromide): 1740 and 1690 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.48 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.54 (fd, J = 2.5, 1H, *H*8 arom), 6.94 (dd, J = 2.5, 8.9, 1H, *H*6 arom), 7.38 (fd, J = 8.2, 2H, *H* arom), 7.57 (s, 1H, =C*H*), 7.59 (fd, J = 8.9, 1H, *H*5 arom), 7.84 (fd, J = 8.2, 2H, *H* arom); ms: (m/e) 427 (M^+).

Anal. Calcd. for $C_{21}H_{17}NO_7S$: C, 59.01; H, 4.01; N, 3.28. Found: C, 59.35; H, 3.84; N, 3.36.

1-Acetyl-2-(2,2,-dimethoxycarbonylvinyl)-3-acetoxyindole (**13a**).

Same procedure as for compound **6** or compound **11** but starting from the crude compound **4a**; compound **13a** was obtained in 68% yield, mp 157°; ir (potassium bromide): 1750, 1730 and 1700 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.36 (s, 3H, $COCH_3$), 2.71 (s, 3H, $COCH_3$), 3.75 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 7.2-7.4 (m, 2H, *H* arom), 7.43 (fd, J = 8.7, 1H, *H* arom), 7.89 (s, 1H, =C*H*), 8.06 (fd, J = 8, 1H, *H*7 arom); ms: (m/e) 359 (M^+).

Anal. Calcd. for $C_{18}H_{17}NO_7$: C, 60.17; H, 4.77; N, 3.90. Found: C, 60.41; H, 4.97; N, 3.79.

1-Acetyl-2-(2,2-dimethoxycarbonylvinyl)-3-*p*-toluenesulfonyloxyindole (**14a**).

Same procedure as for compound **8a** but starting from the crude product **4a**; compound **14a** was obtained in 24% yield, mp 158°; ir (potassium bromide) 1720 and 1700 (CO) cm^{-1}; ^1H nmr (deuteriochloroform): 2.46 (s, 3H, $COCH_3$), 2.65 (s, 3H, $COCH_3$), 3.77 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 7.24 (s, 1H, =C*H*), 7.32 (ft, J = 7.7, 1H, *H* arom), 7.42 (ft, J = 7.7, 1H, *H* arom), 7.67 (fd, J = 8.3, 3H, *H* arom), 7.73 (fd, J = 8.3, 1H, *H* arom), 7.98 (fd, J = 8.3, 2H, *H* arom); ms: (m/e) 471 (M^+).

Anal. Calcd. for $C_{23}H_{21}NO_8S$: C, 58.59; H, 4.49; N, 2.97. Found: C, 58.42; H, 4.72; N, 3.01.

REFERENCES AND NOTES

[1] A. Buzas, C. Hérisson and G. Lavielle, *Synthesis*, 129 (1977).

[2] J. Y. Mérour, J. Y. Coadou and F. Tatibouët, *Synthesis*, 1053 (1982).

[3] A. Buzas and J. Y. Mérour, *Synthesis*, 458 (1989).

[4] P. L. Julian, E. W. Meyer and H. C. Printy, Heterocyclic Compounds, Vol **3**, R. C. Elderfield, ed, John Wiley and Sons, New York, 1952.

[5] R. J. Sundberg, The Chemistry of Indoles, Academic Press, New York, 1970, p 367.

[6] D. Kaminsky and R. I. Meltzer, *J. Med. Chem.*, **11**, 160 (1968).

[7] Y. Tominaga, R. Natsuki, Y. Matsuda and G. Kobayashi, *Chem. Pharm. Bull.*, **21**, 1658 (1973).

[8] M. C. Sacquet, M. C. Bellassoued-Fargeau, B. Graffe and P. Maitte, *J. Heterocyclic Chem.*, **22**, 757 (1985).

[9] J. Y. Mérour and F. Cossais, *J. Heterocyclic Chem.*, **28**, 1875 (1991).

[10] D. L. Boger and M. D. Mullican, *J. Org. Chem.*, **49**, 4033 (1984).

[11] The ^1H nmr signals for the *E* and *Z* isomers.